

THERMODYNAMIC PROPERTIES OF TERPENE HYDROCARBONS

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INTRODUCTION

Dr. F. D. Rossini once said, "The ultimate end of chemical thermodynamics may be said to be the evaluation of the free energies of formation, from the appropriate units of matter, of every substance in every possible state. From the standpoint of the compilation of the ultimate or master table of chemical thermodynamics, the most important thermodynamic properties, in addition to the free energies themselves, are the heat content and the entropy; and the successful evolution of the master table is predicted upon the existence of accurate values of the heats of formation and the entropies of formation."¹

In the long view, this investigation was undertaken to provide one more increment of knowledge to the mass that will be necessary to carry out the compilation of the master table. In the shorter view, it was thought that accurate values of the heats of combustion and isomerization of the common terpene hydrocarbons might be of value to those who are, and will be, concerned in the manufacture of useful products from these compounds.

There has been no attempt to include herein a complete bibliography on the topic of calorimetry. Only those references which have a direct bearing on this investigation have been included.

CHAPTER I

GENERAL DISCUSSION OF COMBUSTION CALORIMETRY

The classical method of determining the heat of combustion of a substance containing only carbon, hydrogen, and oxygen is to explode a sample of the substance in a rigid vessel. This vessel is contained in a suitable amount of water, and the heat evolved is evaluated from the rise in temperature of the water. The rigid vessel which contains the sample is called the bomb. The bomb, the water, and the metallic container for it make up the calorimeter. Since there are no perfect heat insulators, it is necessary to know accurately the heat transfer between the calorimeter and its surroundings. To this end, the calorimeter is enclosed in a jacket whose temperature is known at all times.

Two main methods are used in calorimetric measurements. In one, the temperature of the jacket is kept the same as the calorimeter throughout the combustion. This method has the advantage of eliminating the heat losses between the calorimeter and the jacket. This is of value in processes in which small amounts of heat are evolved over long periods of time.² In the other method, so-called isothermal,³ the jacket is kept at a constant temperature a few degrees above the starting temperature of the calorimeter, and the heat losses are evaluated and corrected for. This method is generally used in fast processes

in which an appreciable amount of heat is liberated. In the present investigation, the isothermal method was used and will therefore be discussed to the exclusion of the adiabatic method.

Energy Equivalent of Calorimeter.—The main source of discrepancy in data reported by different laboratories has been the difficulty of determining the energy absorbed per unit of temperature rise in the installation used. The earliest attempts made use of a knowledge of the kinds and quantity of the material making up the calorimeter in order to arrive at the heat capacity of the system. Absolute measurements of this sort are unsatisfactory in that they neglect factors which are a property of the process rather than the material system.^{4,5} Such things as lags in the thermometric system and calorimeter and heat conduction through the leads are very difficult or impossible to determine absolutely. For this reason a method of comparative measurements is always used in precise work.

In a calibration of this sort the calorimeter serves as an absorber and comparator of the energies released, first in a process which liberates a known amount of heat, and then in the unknown process. The known and the unknown processes are carried out under identical conditions, thereby eliminating the need to make corrections for lags and other unknown factors.

The measurements of electrical resistance and current are subject to accurate determinations and therefore the amount of heat dissipated in a resistor has become the ultimate known process to which others are referred.⁴ This method, however, is a tedious and complicated one. For this reason, work was undertaken to provide a convenient chemical process to which the unknown processes might be referred. Out of this work has come the use of benzoic acid as a combustion standard.^{6,7,8,9} The calibration of a calorimeter then consists in obtaining a standard sample of benzoic acid (provided by the Bureau of Standards), combusting it, and comparing the unknown compounds to the accurately known heat of combustion of benzoic acid. This is the method that was used in this investigation.

Heat Transfer Between Calorimeter and Jacket.--The heat transfer between the calorimeter and the constant temperature jacket which surrounds it is frequently thought of as a correction that must be applied to the observed temperature rise. This conception of it implies that it would be advantageous to make it as small as possible. A better way to view the situation is to consider the total temperature rise of the calorimeter as a sum of two terms. The first is the heat that is given off by the process in the bomb. The second is that heat which is added as a result of the transfer of some heat from the jacket to the calorimeter.

This gives one the correct outlook. It is not so important that the heat transfer contribution be made as small as possible; but rather that one should so specify conditions that it, no matter what the size, may be determined accurately.¹⁰

The heat transfer is generally considered to follow Newton's law. In order that this assumption shall be valid it is necessary to specify certain conditions. Transfer by conduction and radiation are the only ones that follow the law and these only to an approximation. If the thermal head between the calorimeter and the jacket exceeds a few degrees in magnitude the law is no longer valid. Heat also can be transferred by convection and evaporation, which do not depend on the thermal head. Hence, in the design of a calorimeter one must attempt to make the contributions of the latter effects as small as possible. Let us consider them one at a time and see what must be done to minimize the errors in the heat transfer term.

Convection, of all the modes of heat transfer, causes the most trouble. It can, however, be reduced to negligible proportions by proper design of the calorimeter. White¹⁰ has shown that an air gap of approximately one centimeter between the calorimeter and the jacket is consistent with a precision of .01 percent.

Evaporation should cause the least trouble in the installation since it can easily be eliminated. Unless

precautions are taken, however, it can be a serious cause of trouble. The first obvious method of elimination is to enclose the calorimeter liquid completely by means of an appropriate cover. Also one can arrange the experiment so that the jacket temperature is always above that of the calorimeter. This prevents any of the calorimeter liquid from condensing on the walls of the jacket and giving up its heat of condensation to the environment. Any small effects that remain after these precautions are taken can be evaluated and allowed for in the calculations, as will be shown later.

Temperature Measurement.--A great deal of combustion calorimetry in the past has been done using a mercury in glass thermometer of some type or the other. Under the best conditions an accuracy of one part per thousand is the best that can be expected. However, in recent years, the use of resistance methods has considerably improved this accuracy. A platinum resistance thermometer and the associated equipment is undoubtedly the most accurate and reliable method of temperature measurement available. By this means the temperature rise in the calorimeter may be determined to an accuracy of one part in ten thousand.

There is, however, one factor that must be carefully watched for; this is the heating effect in the coil of the thermometer due to the measuring current used. The current must be passed through the coil long enough before each

measurement to be sure that the thermometer has reached equilibrium with the body whose temperature is to be measured. It must also be ascertained that the measuring current remain constant over the entire experiment. The assumption is made that the heating effect in the coil is the same at all temperatures. This is certainly valid over the short range, approximately 2°C. , used in this investigation. Since only differences in temperature are being measured there is no error introduced as long as these effects are kept constant. By the same token it is not necessary to worry about lead resistances as long as the assumption that they are constant over the entire time of the experiment is valid.

Stirring of Calorimeter Liquid.--In order that the temperature sensitive element shall properly record the mean temperature of the calorimeter, the liquid used must be stirred thoroughly. The most efficient method is by means of a screw stirrer, in a vessel which is shaped to adapt it to this type of agitation. A study by E. F. Mueller at the Bureau of Standards¹¹ showed that a body of liquid, containing a central obstruction such as a bomb, reached equilibrium much more quickly using a propellor as a stirrer than when a reciprocating ring stirrer was used. The reciprocating stirrer has the additional disadvantage that a portion of it must leave the liquid thus promoting evaporation. There is a heating effect due to the stirring which is evaluated for

each determination. Here again precautions must be taken so that the assumption that it is constant over the time of the experiment is valid. The method by which this contribution is calculated is considered later.

Determination of the Amount of Reaction.-- The reaction taking place in the bomb must be precisely specified. This can be done by making certain that the substance combusts completely. For compounds containing carbon, hydrogen, and oxygen this means that all the carbon goes to carbon dioxide and all the hydrogen goes to water. Incomplete combustion will evidence itself by a deposit of carbon in the bomb and/or by the presence of carbon monoxide in the products of the combustion. An analysis of the combustion products for carbon monoxide is one means of checking for incomplete combustion.

If one bases the amount of reaction on the weight of the sample placed in the bomb, the inert impurities in the sample such as water and dissolved air are neglected.¹² For this reason it has come to be the practice to base the amount of reaction on the weight of carbon dioxide formed. This eliminates the need of correcting for the dissolved air and water and also allows one to make corrections for small amounts of incomplete combustion.

CHAPTER II

CALORIMETRIC EQUIPMENT AND PROCEDURE

The combustion bomb used in this investigation was of a special design being used at the Bureau of Standards in their combustion work. It was constructed to order in the University of Florida machine shop, using fittings obtained from the Parr Instrument Company. The body and head of the bomb were constructed of illium, a corrosion resistant alloy, obtained from the Illium Corporation in the form of a casting. The head was held in place by a stainless steel cap which screws down over the body of the bomb. A pressure tight seal was made by twelve set screws in the steel cap. These bear down on a pressure ring and effect a closure between the head and the body by means of a teflon gasket. The head of the bomb had two valves to allow it to be filled with oxygen to the proper pressure and to allow it to be flushed out with oxygen. There were also two platinum-iridium electrodes which hold the firing wire to ignite the charge. The bomb had an internal volume of 390 ml. and weighs 4443.5 gms.

Calorimeter.--The calorimeter was made by the Precision Scientific Company according to specifications outlined by the Thermochemical Section of the Bureau of Standards. The calorimeter itself was cylindrical in shape, with an extended part separated from the main portion except at the top and the bottom. This extended portion contained the stirrer and

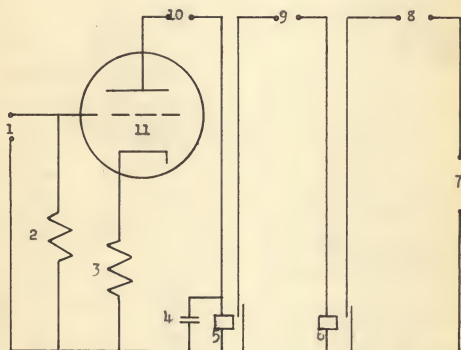
was shaped at the bottom so as to direct the flow of water evenly throughout the calorimeter. The part of the calorimeter above the stirrer was closed except for a hole large enough to admit the stirring shaft. In order to avoid evaporation in so far as possible the main portion of the calorimeter was provided with a cover which had three openings, one for the thermometer and the other two for the leads to the bomb. If temperature equalization is to be achieved this cover must be in contact with the liquid in the calorimeter. It was accordingly built in the form of an inverted dish with collars soldered around the top of the openings. The entire calorimeter was made of nickel plated copper and was highly polished on the outside to reduce radiation effects.

The calorimeter was held in a slightly larger container of the same shape, which could be submerged in a bath of water. The inside surface of this container was highly polished also. The calorimeter was supported by means of three small pegs of a non-conducting material which fit into corresponding indentations on its bottom. These pegs were placed so that the calorimeter was centered in its container with a one centimeter air gap between them at all points. The cover of this outside container was provided with three openings corresponding with the openings in the calorimeter cover and had collars connected to them which extended well above the surface of the surrounding liquid. This cover

also contained the top portion of the stirring shaft, including the bearing surfaces and a connection to a stirring motor by means of a flexible cable. The top part of the stirrer was attached to the bottom part after the cover was in place by screwing them together. The cover of the outside container was held in place by six hand screws and a water tight seal was made against a rubber gasket.

The outside container was actually the constant temperature surface which maintains a known thermal head between it and the calorimeter. It was in turn held in a much larger vessel which contained water at a constant temperature. The constant temperature jacket was fitted with a large stirrer, a coil of metal tubing to provide cooling, and a 250 watt heater. Constant temperature was maintained by means of a toluene bulb and the relay whose circuit is diagrammed in Figure 1, p. 12.

It was found necessary to use two relays in the circuit for the following reason. If the control current of the relay circuit is of any magnitude at all there is some sparking at the mercury surface in the toluene bulb when contact is made. It was found that most sensitive relays which will operate on low currents will not handle enough power to actuate the heater. On the other hand, relays which have large contacts have the disadvantage of requiring much larger currents in the control circuits. As a consequence, two relays



1. Toluene Bulb Contact
2. 1 Megohm Resistor
3. 400 Ohm Resistor
4. 20 Mfd. Condenser
5. 4000 Ohm Relay

6. Commercial Relay
7. Heater Contacts
8. 110 A. C.
9. 110 A. C.
10. 110 A. C.
11. 71-A Radio Tube

Circuit Diagram for Thermostat Control
Figure 1

were used, the smaller of which was actuated by the toluene bulb. This small one in turn handled the control current for a large relay which carried the heaters. This set-up was found to be very effective. If proper balance was achieved between heating and cooling it was possible to attain control to $\pm 0.001^{\circ}$. Even with practically no adjustments beyond a crude equalization of heating and cooling, control to $\pm 0.002^{\circ}$ was attained.

Thermometric System.--The thermometric system consisted of a platinum resistance thermometer and the associated apparatus. The thermometer was of the flat calorimetric type³ and was equipped with four leads. By means of the four leads and a reversing switch in the resistance bridge one can cancel out the lead resistance. However, since only differences in resistance were used in the calculations, it was not necessary to take them into consideration except to assure their constancy. The thermometer had a resistance of about 25.5 ohms at 0.0° C. and a resistance change with temperature of approximately 0.1 ohm per degree C. The resistance of the thermometer at 0.0° C. was checked at intervals throughout the investigation and was found to change by less than 0.00002 ohms over this period (nearly two years). The constants for this thermometer were determined at the Bureau of Standards. The relation between the resistance and the temperature is given by the following equations:

$$R_t = 25.54465 + 0.1060748t - 0.00000058t^2$$

$$dR_t/dt = 0.1060748 - 0.00000116t$$

This conversion formula was used only to find the final temperature of the calorimeter system at the end of a combustion. For the purposes of calculation the actual values of the resistance were used and the energy equivalent of the calorimeter, in J/ohm, was determined directly in terms of the platinum thermometer used.¹⁴

The resistance of the sensitive element was determined with a Mueller Resistance Bridge, expressly designed for use with a platinum resistance thermometer. The bridge balance was found by using a sensitive low resistance galvanometer (L&N HS-2285). The resistance bridge consists of six decades of resistances which will measure a maximum of 111.111 ohms. The sensitivity of the circuit was such that, with a five milliamp current through the thermometer, 0.0001 ohm unbalance gave a deflection of 3 mm. on the galvanometer scale. This means that the temperatures could be read to 0.0001° C. The bridge was calibrated at the Bureau of Standards and the calibration over the range used was checked in this laboratory, by comparing with a standard resistance of 10 ohms which had been calibrated at the Bureau of Standards.

Ignition Energy.--No explicit attempt was made in this investigation to determine the ignition energy. Since

the ignition was performed in the same fashion in both the calibration experiments with benzoic acid and in the unknown combustions, the only assumption made is that the energy imparted to the system by the heating of the ignition wire will remain constant from run to run. This same assumption would have to be made were the energy to be determined in a separate series of experiments. Consequently there was no loss of accuracy by this procedure. A correction was made, however, for the amount of wire actually burned in each experiment using the value 7.5^{14} KJ/gm for the heat of combustion of iron wire. It was found that in a majority of the experiments the wire was completely burned.

Correction for Nitric Acid.--A correction for the nitric acid formed was made using the value 57.8 KJ/gm¹⁴ for the standard heat of formation of nitric acid. The amount of acid formed was determined by titrating the bomb washings with 0.05 N NaOH, using brom-cresol green as an indicator. It was found that the correction for nitric acid remained nearly constant with each tank of oxygen used, but changed considerably from tank to tank.

Purification of Oxygen Used in Combustion.--Commercial oxygen, which was used in this investigation may contain combustible impurities. It was necessary then to purify the oxygen before it could be used in the bomb.¹⁵ For this reason the oxygen which was used to fill the bomb was passed

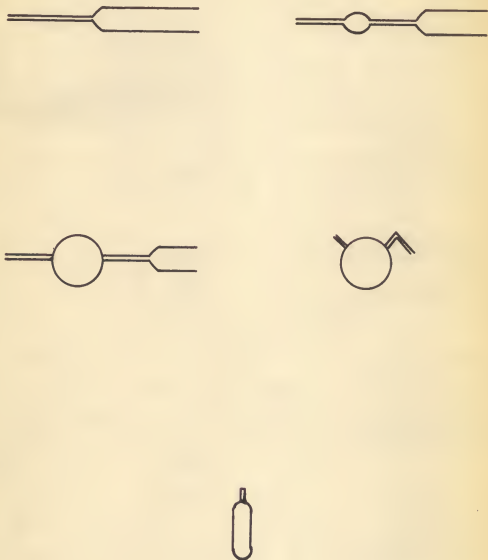
through a stainless steel tube containing copper oxide heated to 500° C.¹³ in order to oxidize any interfering impurities. It was then passed through a tube containing ascarite to absorb any carbon dioxide from the oxidation. Finally the oxygen was admitted to the bomb. The filling proceeded slowly so that it was certain that the oxygen was in contact with the hot copper oxide long enough to completely oxidize any impurities. In these experiments the oxygen was fed into the bomb at such a rate that it took twenty minutes to reach the standard pressure of 30 atmospheres.

Examination of the Products of Combustion.--The products of the combustion were examined for the amount of nitric acid formed as described on p. 15. A determination for the amount of carbon dioxide formed in the experiment was also performed as well as the amount of carbon dioxide formed in the subsequent oxidation of any products of incomplete combustion.

These determinations were made using an absorption train with the carbon dioxide being absorbed in ascarite. Oxygen from a commercial supply was first passed through a tower containing copper oxide at 500° C. and then through a tower of ascarite to purify it as described above. The oxygen passed into the bomb through the inlet valve and out again through the exit. From there it passed to an absorption tube containing ascarite backed with a plug of magnesium perchlorate

which removed all the carbon dioxide formed in the combustion. Next was another tower of copper oxide, like the one described above, to oxidize to carbon dioxide any products of incomplete combustion. This was followed by another absorption tube of ascarite and then the oxygen was passed through a tube containing ascarite and magnesium perchlorate, to prevent back diffusion from the room, and finally through a flow meter to regulate the velocity of flow. The entire train was of glass except for the tygon tubing used to connect the absorption tubes and the metal bomb connections. The flow of oxygen was regulated at 200 ml. per minute by means of the calibrated flow meter.

Sealing Samples in Glass Ampoules.--The compounds that were used in this investigation were all liquid. It was necessary to enclose the samples from air and to prevent any evaporation between the time of weighing and combustion. To accomplish this the samples were weighed in small glass ampoules which were made as follows: A soft glass tube of 4 mm. inside diameter was drawn out into a capillary at one end. It was again drawn out a short distance above the shoulder of the capillary so that a blob of glass was obtained between two capillary tubes, as shown in step 2 of Figure 2, p. 18. The intervening blob of glass was heated until it could be blown into a thin walled bubble. This bubble was broken off from the main portion of the tube and the capillaries bent as shown



Steps in Preparation of Ampoules for Enclosing Bulbs

Figure 2

in step 4 of Figure 2. Since the ampoule was to withstand a pressure of 30 atmospheres the sides of the spherical bubble were flattened by holding them in the flame a moment. This imparted some flexibility to the ampoules so that when they were completely full the pressure was supported by the liquid.¹²

The ampoules were filled by applying a slight suction from a vacuum line to the straight capillary. When it was completely full a filter paper applied to one end will draw the liquid away from the other end far enough so that the capillary can be sealed off in a small flame. After one end is sealed, a piece of ice held to the bottom of the ampoule will draw the liquid from the other end so that it, too, may be sealed. This filling operation may be accomplished in something over one minute.

Prior to filling, the ampoules were weighed under water to arrive at an estimate of their volume so that the proper amount of sample could be used in the experiment. To accomplish this an old analytical balance was modified so that the bouyancy effect of the ampoule when held under water could be balanced by means of brass weights. It was found by trial that a bouyancy effect requiring one gram to neutralize would give the proper volume of sample. Ampoules which were appreciably smaller or larger than this were discarded. The actual range used was from 0.95 gm. to 1.05 gm., which gave

sample weights ranging from 0.90 to 1.00 gm.

Procedure for Combustion Run.--An ampoule to hold the proper amount of sample to give the correct temperature rise was weighed, filled with the sample to be run and weighed again. This sample was placed in the platinum crucible which was held in position immediately below the fuze wire in the bomb. 0.00760 gm. of fuze wire was crimped into position between the electrodes and one ml. of water added to the bomb. The bomb was assembled and a pressure tight seal was made by tightening down the 12 set screws in the cap in the following manner: Designating any one screw at 1, it and the one immediately opposite from it, 1', were tightened; then 4, 4'; 2, 2'; 5, 5'; 3, 3'; and 6, 6'; which completed the circuit. Each screw was tightened three times in the above order until no further tension could be achieved by means of the Allen wrench used. The bomb was connected to the oxygen filling train, both valves were opened and oxygen was allowed to flush through it for 15 minutes at the rate of about 200 ml./min. Then the exit valve was closed and the bomb filled to 30 atmospheres over a period of 20 minutes.

Meanwhile the constant temperature jacket of the calorimeter was being brought up to temperature and adjustments made so that control to $\pm 0.002^{\circ}\text{C.}$ could be achieved. Also during this period the calorimeter water was being brought up to the starting temperature, approximately 24.5°C. ,

and the proper amount of water was being weighed out. It was found that a total weight of calorimeter and water of 5395.00 gms. filled it to the proper point. This weighing was made to 0.05 gm. on a large capacity Metro-gram balance.

After the oxygen in the bomb had reached the proper pressure the valves were closed and the bomb removed from the filling apparatus and the leads attached. The calorimeter was placed in position in the jacket, the bomb carefully lowered into it, and the entire apparatus assembled. After the thermometer had been put in place and the calorimeter stirrer started, about five minutes were allowed for everything to reach equilibrium, and then the combustion run was started.

The run consisted of a 20 minute fore rating period, a 16 minute reaction period and a 20 minute after rating period. The times during the two rating periods and the last 11 minutes of the reaction period were determined by means of a light which flashed on two seconds preceeding each minute and then off exactly on the even minute. Recordings of the galvanometer deflection and its zero were made after each reading and from these and a knowledge of the sensitivity of the galvanometer the exact resistances on the even minutes were determined. On exactly the 20th minute a switch was closed manually. This placed 24 volts A.C. across the firing wire, which became incandescent and started the reaction

period.

From this point and for the next five minutes the readings are made as quickly as possible. The readings are made at even resistance values rather than at even times. Times were recorded using two stop watches, one of which was stopped as the galvanometer indicated zero and the other was started. A precaution here was to make sure that the stop watch which had just stopped was set back to zero before the next reading was made. Time was recorded to the nearest 0.1 second. The readings were made so that the final one in this period fell exactly on the 25th minute.

From 25 to 36 minutes the readings were made every minute, at which time the reaction period was complete. During the after rating period, from 36 to 56 minutes, the readings are again made once every two minutes.

Upon completion of the combustion run the platinum thermometer was transferred from the calorimeter to the jacket and its temperature was recorded. The effect on the thermometer of the very small fluctuations of the jacket temperature were damped out by means of a tube of water extending down into the jacket, and into which the thermometer was placed. This recorded the mean temperature without the need of observing the fluctuations for several minutes and calculating a mean temperature.

During the time that the combustion run was being

made, the analysis train was being flushed out with oxygen and on completion of the combustion the absorption tubes were weighed to 0.02 mg. The bomb was placed in the train, the exit valve opened and the contents of the bomb were allowed to escape at the rate of 200 ml. per minute into the analysis train. When the pressure had reduced to atmospheric, the inlet valve was opened and oxygen was flushed through the system for one hour at the same rate. The absorption tubes were then weighed to determine the amount of carbon dioxide formed in the combustion, and the amount of incomplete combustion, if any, as evidenced by an increase in the weight of the second tube. The amount of firing wire not consumed was weighed and the washings from the bomb titrated with 0.05N NaOH. This completed a combustion run.

On the next three pages are Tables 1 and 2 covering data for one experiment picked at random from the ones that were recorded in this investigation. Table 1 contains observations of time and resistance. The time is recorded in the first column. In the column headed Reading are recorded the decade values from the resistance bridge. The Z column contains the galvanometer zero in millimeters, and the D column is the deflection of the galvanometer in millimeters on the even minutes. It will be noticed that from 20 to 25 minutes the readings are recorded in seconds and as noted before the last reading was taken on exactly the 25th minute.

TABLE 1

OBSERVATIONS FOR HEAT OF COMBUSTION DETERMINATION

Sensitivity -- 2.5 Div/0.0001 ohms JKT -- 28.22820				
Time Min.	Decade Reading Ohms	Z mm.	D mm.	Resistance Ohms
0:00	0.0080	-3 3/4	0	0.00788
2:00	0.0088	✓ 1/4	0	0.00881
4:00	0.0097	0	✓ 1/2	0.00968
6:00	0.0106	0	✓ 2	0.01053
8:00	0.0115	0	✓ 3 3/4	0.01138
10:00	0.0123	0	✓ 2 3/4	0.01221
12:00	0.0131	0	✓ 1 1/4	0.01306
14:00	0.0139	0	0	0.01390
16:00	0.0147	0	-1	0.01473
18:00	0.0156	0	✓ 1 1/4	0.01556
20:00	0.0164	- 1/4	0	0.01639
20:10.3	0.0174
20:29.2	0.0274
20:44.2	0.0474
20:56.4	0.0674
20:68.2	0.0874
20:81.9	0.1074
20:99.1	0.1274
20:114.9	0.1374
20:128.9	0.1474
20:145.9	0.1574
20:166.9	0.1674
20:186.9	0.1724
20:204.6	0.1774
20:226.7	0.1824
20:240.1	0.1854
20:268.7	0.1874
20:288.5	0.1874
20:300.0	0.1898	✓ 1 3/4	-1	0.18989
26:00	0.1940	✓ 2	✓ 2	0.19400
27:00	0.1961	✓ 1 3/4	✓ 3/4	0.19613
28:00	0.1973	✓ 1 1/2	✓ 1 1/2	0.19733
29:00	0.1980	✓ 1 1/2	✓ 1	0.19802
30:00	0.1984	✓ 1 3/4	✓ 1	0.19843
31:00	0.1986	✓ 1 3/4	-1 3/4	0.19872

TABLE 1 -- continued

Time Min.	Decade Reading Ohms	Z mm.	D mm.	Resistance Ohms
32:00	0.1988	$\nearrow 1 \frac{3}{4}$	-1	0.19889
33:00	0.1990	$\nearrow 1 \frac{3}{4}$	$\nearrow 1$	0.19903
34:00	0.1991	$\nearrow 1 \frac{1}{2}$	0	0.19915
35:00
36:00	0.1993	$\nearrow 1 \frac{1}{2}$	0	0.19935
38:00	0.1995	$\nearrow 1 \frac{3}{4}$	$\nearrow 1$	0.19952
40:00	0.1997	$\nearrow 1 \frac{1}{2}$	$\nearrow 2$	0.19968
42:00	0.1998	$\nearrow 1 \frac{1}{2}$	0	0.19985
44:00	0.2000	$\nearrow 1 \frac{1}{4}$	$\nearrow 1 \frac{1}{2}$	0.19999
46:00	0.2002	$\nearrow 1 \frac{1}{4}$	$\nearrow 1 \frac{3}{4}$	0.20015
48:00	0.2003	$\nearrow 1 \frac{1}{2}$	0	0.20032
50:00	0.2005	$\nearrow 1 \frac{1}{4}$	$\nearrow 1$	0.20048
52:00	0.2006	$\nearrow 1 \frac{1}{2}$	- $1 \frac{1}{2}$	0.20063
54:00	0.2008	$\nearrow 1 \frac{1}{2}$	$\nearrow 1$	0.20078
56:00	0.2009	$\nearrow 1 \frac{1}{4}$	-1	0.20094

No values of Z and D were noted for this period as the stop watches were clicked as the indicator crossed the zero so there were no deflections to be noted.

Table 2 contains the data covering the weighing of the sample and the analysis of the products of combustion.

TABLE 2

ANALYTICAL DATA

Sample	
Capsule.....	0.18263 gms.
Capsule / H'.....	1.00882 gms.
H'.....	0.82619 gms.
* 1.0011H' = H	0.82710 gms.
CO ₂ t	2.67200 gms.

Tube 1	
Before	6.10130 gms.
After	8.77050 gms.
CO ₂	2.66920 gms.
* 0.9999CO ₂ = CO ₂	2.66890 gms.

Tube 2	
Before	8.73350 gms.
After	8.73450 gms.
CO as CO ₂	0.00119 gms.

Fe	
Before	0.00760 gms.
After	0.00000 gms.
Used	0.00760 gms.

NaOH	0.60 ml.
Carbon	None
Odor	None
Remarks	

* Correction to Vacuo.

CHAPTER III

CALCULATIONS AND RESULTS

Reduction of Data.--As has been mentioned before, if the proper precautions have been taken in the design of the calorimeter and in the method of making measurements, Newton's law of cooling will express the heat transfer within the limits of experimental error. The law is stated very simply; the rate of heat transfer between two bodies is proportional to the difference of temperature between them. In mathematical terms:

$$(1) \quad dT/dt = k(T_2 - T_1) / w'$$

where T is temperature in $^{\circ}\text{C}.$, t is time in minutes, and k is the cooling constant in min.^{-1} .

The constant term w' allows for those factors which are not dependent on the thermal head, such as the heat of stirring and the effect of evaporation.

Since resistances of the platinum resistance thermometer are nearly linearly related to temperatures, Newton's law can be assumed to hold for them also and the above equation in terms of resistances can be written as follows:

$$(2) \quad dR/dt = k(R_2 - R_1) / w$$

where k is the cooling constant of the calorimeter, and the R 's are the resistances in ohms.

Three equations can be written, one each for the three periods of the combustion:

$$(3) \quad S_{10} = k(R_j - R_{10}) / w$$

$$(4) \quad S_r = k(R_j - R_r) / w$$

$$(5) \quad S_{46} = k(R_j - R_{46}) / w$$

In these equations S_{10} is the resistance change per minute in the fore period obtained from the relation $(R_{20} - R_{10})/20$. R_j is the resistance of the thermometer when measuring the temperature of the jacket. R_{10} is the mean resistance during the fore period, which is the resistance at the 10th minute. S_r is the resistance change during the reaction period and R_r is the mean resistance during the reaction period, both of which must be evaluated. S_{46} and R_{46} stand in the same relation to the after period as do the quantities S_{10} and R_{10} with respect to the fore period.

The mean resistance during the reaction period is found from the integral over the reaction period:

$$(6) \quad R_r = \int_{10}^{36} R dt / 16$$

Substituting this value into equation (4), we have:

$$(7) \quad S_r = k(R_j - \int_{10}^{36} R dt / 16) / w$$

or rearranging:

$$(8) \quad 16S_r = k(16R_j - \int_{10}^{36} R dt) / 16w$$

The quantities k and w can be evaluated from the two rating periods as follows:

Subtracting equation (5) from equation (3) gives:

$$(9) \quad S_{10} - S_{46} = k(R_j - R_{10}) - k(R_j - R_{46}).$$

Rearranging and solving for k gives:

$$(10) \quad k = (S_{10} - S_{46}) / (R_{46} - R_{10})$$

And from equation (5):

$$(11) \quad w = S_{46} - k(R_j - R_{46})$$

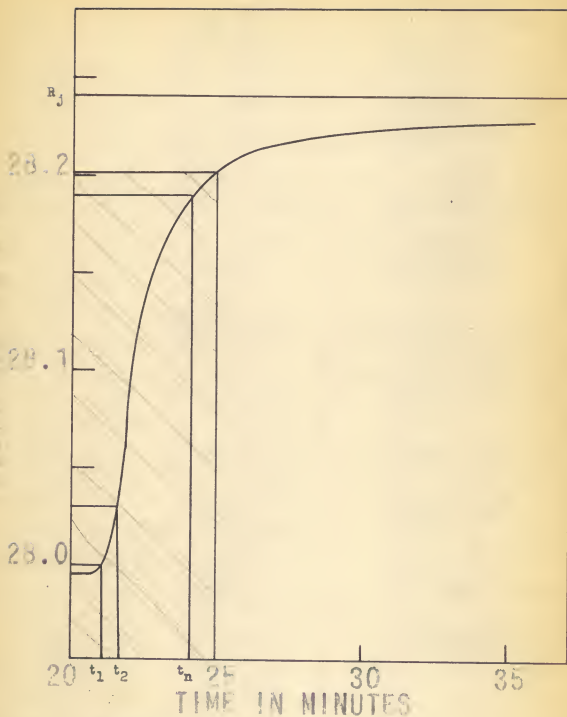
Having now evaluated k and w there remains only one quantity, R_T , to be found in equation (4) before a solution for the resistance change due to the heat transfer between the jacket and calorimeter during the reaction period is obtained. This can be accomplished by integrating equation (6). In Figure 3, p. 30, is plotted t vs R for the reaction period. It is seen that if the area over the curve between 20 and 25 minutes is subtracted from the shaded area and this difference added to the area under the curve from 25 to 36 minutes, we will have exactly the area under the curve from 20 to 36 minutes which is $\int R dt$.

The shaded portion is equal to $(t_{25} - t_{20})(R_{25} - R_{20})$ the area over the curve from 20 to 25 minutes is evaluated by the following formula:

$$(12) \quad \int_{t_0}^{t_n} R dt = \sum_{i=1}^n \Delta R_i t_i = (R_1 - R_{20})(T_1/2) + \\ (R_2 - R_1)(T_2 - T_1/2) + \dots + \\ (R_{25} - R_n)(T_{300} - T_n/2)$$

where R_1 , R_2 , and R_n are the first, second and last readings after the 20th minute and before the 25th minutes. T_1 , T_2 , and T_n are the corresponding times in seconds.

This equation was evolved by the author as a modi-



Time Temperature Curve for Reaction Period

Figure 3

fication of the trapezoidal rule to adapt it to the unequal time increments which were taken during this period. The area calculated using it was checked a number of times by plotting and counting squares. The areas determined by the two methods checked each time within experimental error.

The area under the curve from the 25th minute to the 36th minute was evaluated by the following formula:

$$(13) \sum_{25}^{36} R \cdot \Delta t = (1/2 R_{25} + R_{26} + R_{27} + \dots + 1/2 R_{36})$$

which is the well known trapezoidal rule and is used here because the time increments are equal.

The total resistance difference during the reaction period is $R_{36} - R_{20}$, the resistances at the start and the end of the reaction period. In order to find the resistance change due to the combustion of the charge, it is necessary to subtract from this quantity the heat transferred from the jacket to the calorimeter. This latter quantity, as shown and evaluated above, is $16S_p$. In the calculations as presented in the tables of data, the first item on the right hand side of equation (4), $k(R_j - R_p)$ is called K , and the term $16w$ is called U . Then the corrected resistance rise is:

$$(14) \Delta R_c = R_{36} - R_{20} - K - U$$

The corrected resistance rise calculated above has several more corrections that must be applied to it before it can be said to have any significance as a measure of the

heat liberated by the compounds combusted.

From the data on benzoic acid, it is possible to calculate a rough energy equivalent for the calorimeter system. Using this rough value we can then translate the heat added by the firing wire and the formation of nitric acid into resistance units of the platinum thermometer used. Referring to Table 3, p. 34, we see that benzoic acid has a corrected resistance rise of 0.050199 ohm/gm. of carbon dioxide formed. This is equal to 0.12640 ohm/gm. of acid burned. The accepted value for the heat liberated per gram of acid burned is 26,433.8 int. J./ohm.^{16,17,18} From these values it is easy to calculate that it takes 209,097 int. J. to raise the resistance of the thermometer 1 ohm.

The heat added to the system by the combustion of the firing wire was taken to be 7.5 Kj./gm.¹⁴ Therefore, the correction to be subtracted from the value of ΔR_c calculated above was $\Delta R_1 = (7.5 \times \text{gms. wire burned} \times 1000) / 209,097$.

The heat added to the system by the formation of nitric acid from its elements was taken to be 57.8 Kj./mole.¹⁴ The correction to be subtracted for its formation is therefore:

$$\Delta R_N = (\text{ml.} \times N \times 57.8) / 209,097$$

when N is the normality of the NaOH used. When these corrections have been applied, a value of the resistance change per gm. of carbon dioxide formed is calculated. These values together with the significant steps in the calculations are

listed in Tables 3 through 9, pp. 34 through 40. For a more complete tabulation of the steps in the calculations see Tables 17 through 23, pp. 78 through 85.

Reduction to Standard Conditions.--The calculations and discussion up to this point have considered the process that is taking place in the bomb at the conditions prevailing there. A more useful thermodynamic quantity is the heat released when the reactants and products are in their standard states at a chosen temperature. The final temperature was taken to be 26.5°C. , and the heat of reaction was calculated at this temperature. The standard states of solids and liquids are taken to be pure solid or liquid at a pressure of one atmosphere and at any chosen temperature. Gases are considered in their standard states at zero pressure.

The initial states of the reactants in the bomb at a temperature of 26.5°C. are as follows:

A.--A gaseous phase consisting of oxygen, a small amount of nitrogen, and water vapor at pressure p_1 .

B.--A liquid phase consisting of the sample, at a pressure p_1 .

C.--A liquid phase consisting of water with oxygen and a small amount of nitrogen dissolved in it. The energy of solution of the oxygen and nitrogen are negligible so the phase can be considered to be n' moles of pure water

TABLE 3

DATA ON BENZOIC ACID

Experiment Number	Mass of CO ₂ gms.	k min. ⁻¹	K ohms	U ohms	ΔR_1 ohms
1	4.04519	0.00179	0.00013	0.00032	0.00022
2	3.97604	0.00178	0.00215	0.00039	0.00021
3	3.74097	0.00178	0.00222	0.00041	0.00021
4	3.76588	0.00173	0.00130	0.00057	0.00022
5	3.78400	0.00179	0.00128	0.00047	0.00016

Experiment Number	ΔR_n ohms	$\Delta R_c / CO_2$	Deviation of Mean
1	0.00003	0.50113	0.00007
2	0.00004	0.50113	0.00007
3	0.00000	0.50093	-0.00013
4	0.00000	0.50112	0.00006
5	0.00002	0.50095	-0.00010

Mean	0.050105
Standard Deviation of the Mean	0.000010

TABLE 4

DATA ON β -PINENE

Experiment Number	Mass of CO ₂ gms.	k min. ⁻¹	K ohms	U ohms	ΔR_1 ohms
1	2.77750	0.00183	0.00270	0.00045	0.00027
2	2.80456	0.00175	0.00462	0.00059	0.00025
3	2.68398	0.00192	0.00196	0.00059	0.00027
4	2.83760	0.00192	0.00060	0.00047	0.00027
5	3.06250	0.00193	0.00128	0.00034	0.00027
6	2.84102	0.00187	0.00141	0.00066	0.00021

Experiment Number	ΔR_n ohms	$\Delta R_c / CO_2$	Deviation of Mean
1	0.00000	0.067488	0.000015
2	0.00000	0.067492	0.000019
3	0.00001	0.067488	0.000015
4	0.00002	0.067451	-0.000022
5.	0.00001	0.067451	-0.000022
6	0.00001	0.067469	-0.000004

Mean	0.067473
Standard Deviation of Mean	0.000019

TABLE 5

DATA ON MYRCENE

Experiment Number	Mass of CO ₂ gms.	k min. ⁻¹	K ohms	U ohms	ΔR ₁ ohms
1	3.03047	0.00181	0.00126	0.00057	0.00027
2	2.66890	0.00184	0.00152	0.00045	0.00027
3	2.83050	0.00181	0.00169	0.00026	0.00025
4	2.75632	0.00178	0.00196	0.00058	0.00027
5	3.17430	0.00182	0.00166	0.00060	0.00019

Experiment Number	ΔR _n ohms	ΔR _c /CO ₂	Deviation of Mean
1	0.00003	0.067695	-0.000014
2	0.00001	0.067709	0.000000
3	0.00002	0.067719	+0.000010
4	0.00001	0.067724	+0.000015
5	0.00001	0.067700	-0.000009

Mean	0.067709
Standard Deviation of Mean	±0.000012

TABLE 6

DATA ON ALLO-OCIMENE

Experiment Number	Mass of CO ₂ gms.	k min. ⁻¹	K ohms	U ohms	ΔR_1 ohms
1	2.72452	0.00185	0.00188	0.00037	0.00020
2	2.98010	0.00180	0.00114	0.00044	0.00027
3	3.17092	0.00184	0.00064	0.00038	0.00027
4	3.36110	0.00183	0.00083	0.00032	0.00027
5	2.71720	0.00176	0.00155	0.00038	0.00022

Experiment Number	ΔR_n ohms	$\Delta R_c / CO_2$	Deviation of Mean
1	0.00001	0.067290	-0.000003
2	0.00003	0.067286	-0.000006
3	0.00001	0.067299	+0.000007
4	0.00002	0.067332	+0.000037
5	0.00002	0.067260	-0.000033

Mean	0.067293
Standard Deviation of Mean	± 0.000029

TABLE 7

DATA ON α -PINENE

Experiment Number	Mass of CO ₂ gms.	k min. ⁻¹	K ohms	U ohms	ΔR_1 ohms
1	2.89466	0.00185	0.00244	0.00046	0.00019
2	2.97137	0.00184	0.00204	0.00054	0.00022
3	3.18004	0.00181	0.00211	0.00039	0.00024
4	3.55890	0.00183	0.00090	0.00049	0.00027
5	3.48047	0.00185	0.00087	0.00062	0.00027

Experiment Number	ΔR_2 ohms	$\Delta R_c / CO_2$	Deviation of Mean
1	0.00001	0.067392	0.000015
2	0.00001	0.067382	0.000005
3	0.00001	0.067368	-0.000009
4	0.00002	0.067369	-0.000008
5	0.00003	0.067372	-0.000005

Mean	0.067377
Standard Deviation of Mean	0.000010

TABLE 8

DATA ON LIMONENE

Experiment Number	Mass of CO ₂ gms.	k min. ⁻¹	K ohms	U ohms	ΔR_1 ohms
1	3.05989	0.00182	0.00080	0.00042	0.00027
2	3.24917	0.00176	0.00112	0.00054	0.00027
3	3.54780	0.00191	0.00069	0.00027	0.00027
4	3.12560	0.00196	0.00130	0.00024	0.00027

Experiment Number	ΔR_1 ohms	$\Delta R_c / CO_2$	Deviation of Mean
1	0.00003	0.067008	+0.000010
2	0.00003	0.066988	-0.000010
3	0.00003	0.066999	+0.000001
4	0.00003	0.066998	0.000000

Mean	0.066998
Standard Deviation of Mean	± 0.000008

TABLE 9

DATA ON DIPENTENE

Experiment Number	Mass of CO ₂ gms.	k min. ⁻¹	K ohms	U ohms	ΔR_1 ohms
1	3.4193	0.00183	0.00105	0.00022	0.00027
2	3.4605	0.00177	0.00018	0.00038	0.00027
3	3.45355	0.00181	0.00117	0.00046	0.00025

Experiment Number	ΔR_n ohms	$\Delta R_c / CO_2$	Deviation of Mean
1	0.00003	0.066958	-0.000007
2	0.00003	0.066961	-0.000004
3	0.00003	0.066975	+0.000010

Mean	0.066965
Standard Deviation of Mean	± 0.000009

at a pressure of p_1 atmospheres.

The states of the substances in the bomb after the combustion, all at a temperature 26.5°C. , are as follows:

D.--A gas phase consisting of a mixture of oxygen, nitrogen (negligible for compounds not containing nitrogen), carbon dioxide, and water vapor at pressure p_2 . The water vapor will be considered separately, and the oxygen, the nitrogen, and the carbon dioxide together.

E.--A liquid phase, at pressure p_2 , consisting of an aqueous solution of nitric acid containing dissolved carbon dioxide, oxygen, and nitrogen. The amounts and energies of solution of the oxygen and the nitrogen can again be ignored, but the amount and energy of solution of the carbon dioxide must be considered.

In order to calculate the difference in energy between the bomb process and the standard reaction, the following quantities must be evaluated:

1.--The change in energy, Δu_1 , of r_1 moles of oxygen from zero pressure to p_1 atm.

This is calculated from a knowledge of the Joule-Thompson Coefficient and the heat capacity of oxygen by means of the formula: $(dH/dP)_T = -u_C p$

$$\Delta u_1 = -6.57 p_1 r_1$$

2.--The change in energy of a mixture of r_2 moles of oxygen, s_2 moles of nitrogen, and q_2 moles of carbon

dioxide from p_2 to zero pressure. This is evaluated in the same way as the quantity above and the equation at $T_f = 26.5^\circ \text{C.}$ is:

$$\Delta u_2 = (6.57R_2 + 6.01S_2 + 28.7Q_2 - 11.1Q_2R_2) \\ \times p_2(r_2 + s_2 + q_2)$$

where $R_2 = r_2/(r_2 + s_2 + q_2)$ is the mole fraction of the oxygen, S_2 of the nitrogen, and Q_2 that of the carbon dioxide. S_2 will be negligible for non-nitrogen compounds.

3.--The energy of condensation of $(m_2 - m_1)$ moles of water:

$$\Delta u_3 = -41480 (m_2 - m_1)$$

where m_2 is moles of H_2O after combustion and m_1 is moles of H_2O added before combustion.

4.--The energy of vaporization of q_2^1 moles of carbon dioxide from m_2^1 moles of water.

$$\Delta u_4 = 16900q_2^1$$

where 16900 is the negative of the heat of solution of one mole of carbon dioxide in enough water to produce a saturated solution.

5.--The difference in energy of the liquid $\text{C}_{10}\text{H}_{16}$ at one atm. and approximately 30 atms. is negligible.

6.--The differences in the energy of m' moles of liquid water at 30 atms. and at one atm.; m_1 moles of gaseous water at p_w , the partial pressure of the water and at zero pressure; m_2^1 moles of liquid water at one atm. and 30 atms.;

and n_2 moles of gaseous water at zero pressure and p_v atms. are negligible.

7.--Effect of nitric acid on the vapor pressure of the water and the energy of dilution of the nitric acid by the water (the value 57.8 Kj./mol. is considered to apply) is neglected for these compounds as they do not contain nitrogen.

The corrections described above were calculated on the basis of a sample weight of 0.92000 gm. and a final temperature of 26.5° C. These values were subtracted from the heat liberated in the combustion process. Thus are obtained values of the heats of combustion at constant volume and 26.5° C. as shown in Table 10, p. 48.

The heat of combustion of benzoic acid reported in the literature has been corrected to standard conditions and 25° C. It is necessary, therefore, to convert that value to the conditions that apply in the experiments before it is used to calculate the energy equivalent of the calorimeter. This entails applying the above corrections in reverse to the reported value of the heat of combustion of benzoic acid.

The accepted value of the heat of combustion of solid benzoic acid at 25° C. and one atm. is 26433.8 \pm 2.6 j./gm.^{16,17,18} When this is corrected to bomb conditions of 26.5° C. and 30 atms., it becomes 26423.4 \pm 2.6 j./gm.

Using this value we can now calculate a correct energy equivalent for the calorimeter. Referring to Table 3, p. 34, we see that the benzoic acid causes a rise in the resistance of the platinum thermometer of 0.050105 ohms/gm. carbon dioxide formed. Dividing this number into the corrected value of the heat of combustion of benzoic acid given in the last paragraph, we get for the corrected energy equivalent of the calorimeter, after including a term to convert from gms. of carbon dioxide to benzoic acid, 209050 ± 18 j./gm.

In order to calculate the heat liberated in the bomb process for the compounds investigated, the corrected resistance rise for the compound was multiplied by the energy equivalent of the calorimeter and a factor to convert from gms. of carbon dioxide to gms. of sample. After this value was obtained it was corrected by the methods outlined above to standard conditions and 25° C. These calculations are given in detail below.

Calculations for the Reduction to Standard Conditions.

Initial pressure = 30 atms. Sample weight = 0.92000 gm.

Bomb volume = 388 ml. T_f = 26.5° C.

Number of moles of oxygen in bomb at initial pressure:

$$r_1 = (30 \times 0.386)/(299.5 \times 1.982) = 0.470 \text{ moles}$$

Then:

$$\Delta u_1 = -6.75 \times 30 \times 0.470 = -92.64 \text{ j.}$$

The number of moles of carbon dioxide formed in the combustion,

q_2 , is 10_{n_1} , where n_1 is the number of moles of sample burned and 10 is the number of atoms of carbon dioxide in one molecule of the sample.

$$q_2 = (10 \times 0.92000)/136.32 = 0.0729 \text{ mols.}$$

r_2 , the number of moles of oxygen in the bomb after the combustion is equal to r_1 minus the number of moles of carbon dioxide formed.

$$r_2 = r_1 - 0.0729 = 0.397$$

The volume in the bomb after the combustion, V_2 , equals the bomb volume minus the water formed in the combustion and the water originally in the bomb.

$$V_2 = v - 0.001 - 0.018 \times 8 \times 0.0729 = 0.386 \text{ l.}$$

p_2 , the pressure in the bomb after the combustion is,

$$p_2 = (R_2 + Q_2)(RT)/V_2 = 29.92 \text{ atm.}$$

R_2 , the mole fraction of oxygen in the bomb after the combustion is,

$$R_2 = r_2/(r_2 + q_2) = 0.844$$

and Q_2 , the mole fraction of carbon dioxide in the bomb after the combustion is,

$$Q_2 = q_2/(r_2 + q_2) = 0.156$$

Then,

$$\begin{aligned} \Delta u_2 &= (6.57 \times 0.844) + (28.75 \times 0.156) \\ &\quad - (11.1 \times 0.132) \times 29.92 \times 0.470 \\ &= + 120.40 \text{ J.} \end{aligned}$$

n_1 , the amount of water vapor in the bomb before the combustion

is,

$$\begin{aligned} m_1^i &= (14.0 / 0.043 \times 30) 10^{-4} \times 0.386 \\ &= 0.00059 \text{ mols.} \end{aligned}$$

m_2^i , the amount of water vapor in the bomb after the combustion is,

$$\begin{aligned} m_2^i &= (14.0 / 0.043 \times 0.21 \times 0.156 \times 29.92) 10^{-4} \\ &\times 0.386 = 0.00063 \end{aligned}$$

Then,

$$\Delta u_3 = -41480(m_2 - m_1) = -1.50 \text{ j.}$$

q_2^i , the amount of carbon dioxide dissolved in the water in the bomb after the combustion is,

$$\begin{aligned} q_2^i &= 5.26 \times 6.3 \times 10^{-4} \times 29.92 \times 0.156 \\ &= 2.7 \times 10^{-4} \text{ moles} \end{aligned}$$

Then,

$$\Delta u_4 = 16900 \times 2.7 \times 10^{-4} = / 4.56 \text{ j.}$$

In addition to these corrections, a decrement in energy to convert to heat of combustion at constant pressure must be allowed for through the relation:

$$\Delta H_c(p) = \Delta H_c(v) - \Delta nRT$$

where n is the change in the number of moles of gaseous products and reactants in the bomb process.¹²

$$\Delta n = b/4$$

where b is the number of atoms of hydrogen in one molecule of the sample (in this case 16),

Then,

$$\Delta H_c(p) = \Delta H_c(v) - 4RT = \Delta H_c(v) - 2.374 \text{ Kcal./mol.} ?$$

Another term, $P\Delta V$, should be subtracted to allow for the change in volume of the solid or liquid products. In this case it is negligible since the same volume of water is formed as sample burned in the combustion.

In Table 10 are given values of the heat released in the bomb process, called Q ; then values of the heat of combustion at constant volume and 26.5° C . Next are given the heats of combustion at constant pressure and 26.5° C ., and finally the heats of combustion at 25° C . as calculated from the relation,

$$\Delta H_c(25^\circ \text{ C.}) = \Delta H_c(26.5^\circ \text{ C.}) + \Delta C_p \Delta T$$

where ΔC_p is the difference in the heat capacity of the products and the reactants.

$$\Delta C_p = C_p(\text{CO}_2) + C_p(\text{H}_2\text{O}) - C_p(\text{C}_{10}\text{H}_{16})$$

Lacking precise data, the heat capacity of the $\text{C}_{10}\text{H}_{16}$ was taken to be 59.6 Kcal./mol. ¹⁹ An investigation now in progress in this laboratory should provide precise values of the heat capacities of these compounds in the near future and permit a recalculation of the correction to 25° C . if considered necessary. It is thought, however, that the values will probably be near to the one given here and due to the smallness of the correction a recalculation will not be necessary.

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The value of C_p for liquid water was taken to be 18.0

cal./mol. and C_p for gaseous carbon dioxide taken to be 8.68 cal./mol.²⁰

Then,

$$\Delta H(p)_{25^\circ} = \Delta H(p)_{26.5^\circ} - 0.265 \text{ Kcal./mol.} ?$$

TABLE 10

VALUES OF THE HEATS OF COMBUSTION

$\Delta H_p(26.5^\circ) ?$
column missing

Compound	Q J./gm.	$\Delta H_v(26.5^\circ\text{C.})$ Kcal./mol.	$\Delta H_p(25^\circ\text{C.})$ Kcal./mol.
β -pinene	45567.8 \pm 8.6	1482.9 \pm 0.28	1485.4 \pm 0.34
Myrcene	45729.1 \pm 4.6	1488.2 \pm 0.14	1490.7 \pm 0.24
Allo-ocimene	45448.1 \pm 11.3	1479.0 \pm 0.36	1481.5 \pm 0.43
α -pinene	45503.0 \pm 4.5	1480.8 \pm 0.15	1483.3 \pm 0.25
Dipentene	45247.8 \pm 4.1	1472.5 \pm 0.13	1475.0 \pm 0.24
d-Limonene	45225.2 \pm 3.6	1471.7 \pm 0.11	1474.2 \pm 0.27

The uncertainties in the last column of Table 10 were obtained from the square root of the sum of the squares of the uncertainty in the calorimetric observations, the uncertainty in the energy equivalent of the calorimeter, a 0.01 percent uncertainty in the reduction to standard conditions, and an uncertainty in the purity of the sample where necessary. (See p. 62)

CHAPTER IV

SOURCE AND PURITY OF THE COMPOUNDS

The α -pinene and the β -pinene used in this investigation were obtained from The Glidden Company of Jacksonville, Florida. They were purified by a fractional distillation through a 120 plate column of the Lecky-Ewell type at reduced pressure.²¹ The purified α -pinene had a refractive index of 1.4631 at 25° C. and the β -pinene had a refractive index of 1.4768 at 25° C.

δ -Limonene was obtained from "Stripper Oil", an extract of orange peel, through the courtesy of the Minute-Maid Corporation of Plymouth, Florida. It was carefully fractionated and the purified compound had a refractive index of 1.4701 at 25° C.

Myrcene was obtained from The Glidden Company of Jacksonville. After careful fractionation the compound had a refractive index of 1.4680 at 25° C.

Allo-ocimene and dipentene were obtained from the vapor phase pyrolysis of α -pinene.²² After purification by fractional distillation, they had refractive indices, at 25° C., of 1.5420 and 1.4701 respectively.

The refractive indices reported above check those reported in the literature.²³ However, as a further check on their purity, some freezing point curves were obtained. These curves, together with the experimental procedure and

the method of estimating the purity will now be discussed.

According to the phase rule, a pure liquid at constant pressure will, when the second phase starts crystallizing out, have no degrees of freedom. This means that the temperature of the system must remain constant until the liquid phase has completely disappeared. An impure liquid, on the other hand, has no such restriction and the temperature is allowed to drop during the process of freezing. When the liquid contains an impurity, if the assumption is made that the impurity remains in the liquid phase, that phase becomes progressively more impure as crystallization proceeds. From simple thermodynamic considerations it follows that as a liquid becomes more impure, the freezing point progressively decreases. The size of the depression in the freezing point in relation to the fraction crystallized is a measure of the quantity of impurity present. If some simplifying assumption is made or if the impurity is in such small concentration that the system behaves ideally, it is possible to estimate the amount of impurity from the measured freezing point lowering.

Experimental Procedure.--The sample, whose purity was to be determined, was placed in a small double walled freezing point tube. The tube was equipped with a reciprocating stirrer operating at 120 strokes a minute. Temperature measurements were made with the same apparatus used in the

calorimetric measurements, except that a glass enclosed, round platinum thermometer was used instead of the flat, metal-enclosed one. The sensitivity of the thermometer system was such that the temperature could be read to 0.0005 degrees. An experiment was performed as follows:

The freezing point tube was prepared by carefully washing it and drying with nitrogen. It was placed in position with the stirrer centered in the inside tube. The thermometer was supported in position in the center of the tube by means of a cork, which also had holes to admit the stirrer and to provide an opening through which the sample could be seeded to induce crystallization. After the apparatus had been assembled it was flushed out with nitrogen for 15 to 20 minutes and then the cooling bath was placed in position around the freezing point tube. A 50 ml. sample was pipetted into the tube with the nitrogen still flowing. The flow of dry nitrogen was continued during the entire experiment. This accomplished two purposes. First, it protected the sample from the action of oxygen in the air, and secondly, it kept atmospheric water vapor from condensing in the sample and thereby contaminating it.

The stirrer was started and the sample allowed to cool down to within ten degrees of the freezing point. At this time a vacuum pump, which was connected to the annular space between the walls of the freezing point tube was started, and

this space partially evacuated. This slowed the heat transfer between the sample and the cooling bath down to a point where the sample would crystallize sufficiently slowly to maintain equilibrium. The amount of evacuation was varied so that the temperature change of the sample would be about one degree per minute in the neighborhood of the freezing point.

At about five degrees above the freezing point readings of temperature and time were started and taken approximately every two minutes. When the freezing point was reached crystallization was induced in the sample. This was done in one of the following ways. When liquid nitrogen was being used as a cooling bath a small metal rod was immersed in the nitrogen and then immediately transferred to the sample. This lowered the temperature in the immediate vicinity of the rod and formed some crystals there, which induced the freezing process. When solid carbon dioxide was used as a cooling bath some crystals were prepared separately and introduced on the coiled end of a thin wire. These crystals were obtained by cooling a sample of the compound to the point where it would crystallize. Since they supercool greatly an ordinary bath of solid carbon dioxide did not suffice to solidify them. For this reason the following device was used. The sample was placed in a tube in a bath of solid carbon dioxide. A smaller tube containing powdered solid carbon dioxide was in-

mersed in the sample and this smaller tube placed under reduced pressure. This lowered the temperature sufficiently so that crystals were formed which could then be kept indefinitely in an ordinary solid carbon dioxide bath.

After recovery from supercooling was complete, readings of the time and temperature were taken approximately every minute until the stirrer started laboring heavily at which time the experiment was complete. The cooling bath was removed and the sample allowed to warm up until all the crystals had melted.

Then using a small pipette graduated to 0.1 ml., a known amount of impurity was added to the sample and the same curve was run again under similar conditions.

Estimation of the Amount of Impurity.--Due to several factors, the estimation of the amount of impurity is subject to rather large uncertainties. In the first place, of the compounds investigated, four of them, α -pinene, β -pinene, d-limonene, and dipentene are optically active. It is, therefore, proposed that the optically active isomers are not homogeneous with respect to cryoscopic measurements. One optically active isomer will act as an impurity in the other, or if a racemic compound is formed, an excess of one or the other isomer will act as an impurity in the racemic compound. Also, two of the compounds investigated, allo-ocimene and myrcene, are not optically active but may exist as geomet-

ric isomers, one of which will act as an impurity in the other with respect to cryoscopic measurements. Another obstacle in the path of accurate measurements is the fact that the compounds do not crystallize well. As a matter of fact, it was impossible to induce crystallization in myrcene down to liquid nitrogen temperatures and therefore it could not be investigated for purity by this method. However, the behavior of the compounds, excepting myrcene, at their freezing points together with data on the rotatory power of the particular compound investigated allows a fairly good estimation of the purity.

The method of estimating the amount of impurity was as follows:²⁴

If the system behaves ideally then the amount of depression with a given amount of solvent crystallized is proportional to the amount of impurity present in the sample. In this method, two curves are run; one on the pure material and another on the material with a known amount of impurity in it. Then, designating the freezing curve of the pure material as (I), and the deliberately contaminated sample as (II), we can write the following relation:

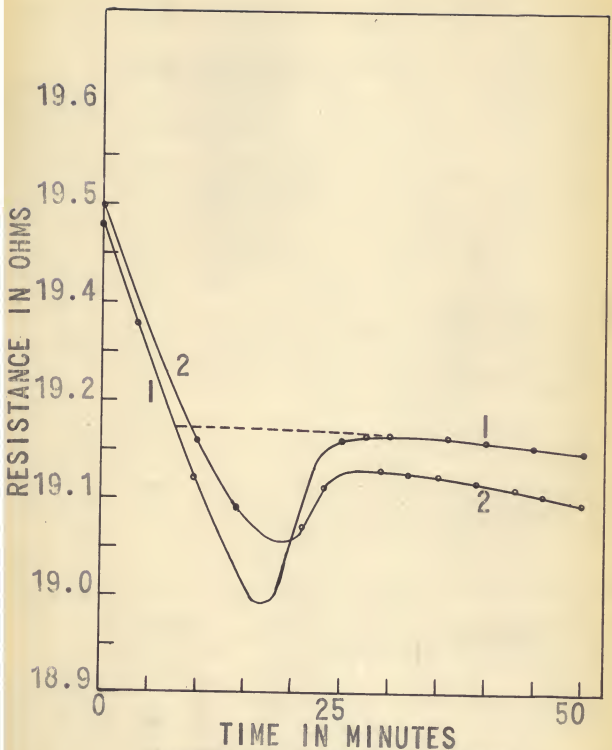
$$\Delta T_I / \Delta T_{II} = X / (X + A)$$

where ΔT_I is the temperature difference between two appropriate points on curve (I) and ΔT_{II} is the temperature difference between two points on curve II, each difference cor-

responding to the same fraction of material crystallized. X is the amount of impurity in the "pure" sample and A is the amount of contamination deliberately added.

In actual practice the cooling curves are plotted and the time that freezing would have started, t_0 , is found by extrapolating the equilibrium portion of the curve back to the cooling curve for the liquid. Then assuming that the rates of crystallization are the same in both cases, two points on each curve are chosen at equal times from t_0 , making sure that they fall on the portion of the curve after recovery from supercooling. The temperature difference between the two points on each curve give the values of ΔT_I and ΔT_{II} . The amount of impurity A , is known and X , the amount of impurity in the original sample, can be calculated. This method has some advantages over others in use,²⁵ in that a knowledge of the heat of fusion is not needed and it is not necessary to know explicitly the fraction of the sample crystallized at any one time.²⁴ On the other hand it has the very great disadvantage that a carefully purified sample is deliberately ruined to get the data. Fortunately, in this investigation sufficient quantities of the materials were on hand to allow such prodigal methods.

Listed in Table 11, p. 61, are values of the ΔT_I and ΔT_{II} taken from the graphs included in Figures 3 to 7. Also in Table 11 are A , the known amount of impurity in mol. fraction

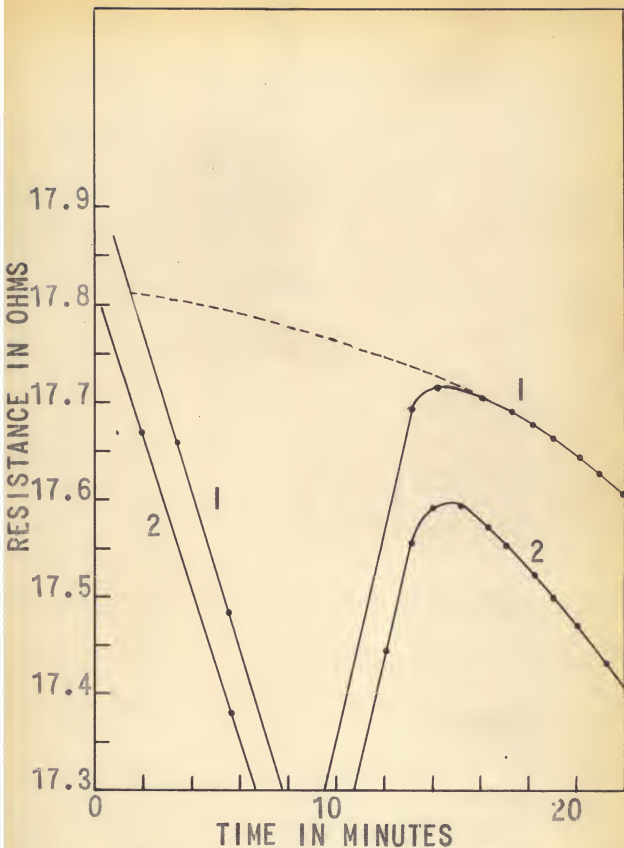


Freezing Point Diagram for Beta-pinene

1. Pure

2. 1.0 mol.% α -pinene

Figure 4

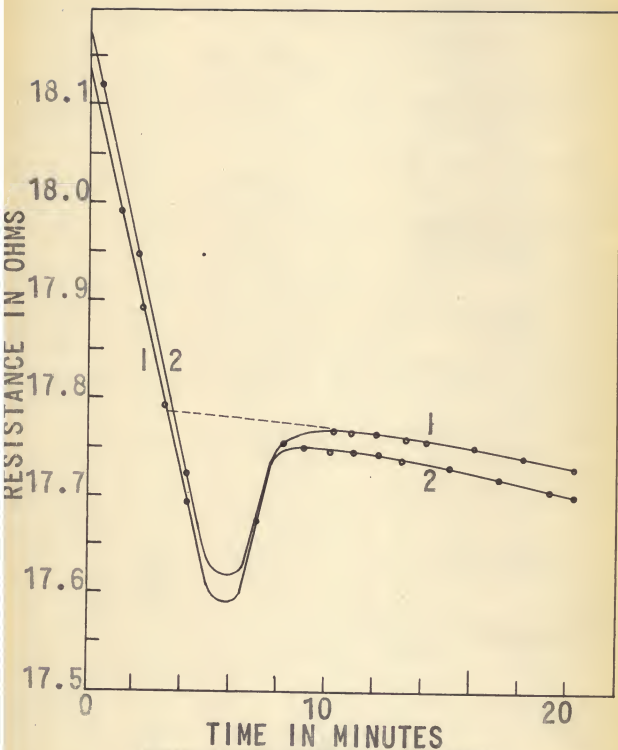


Freezing Point Diagram for Alpha-pinene

1. Pure

2. 1.0 mol.% d-Limonene

Figure 5

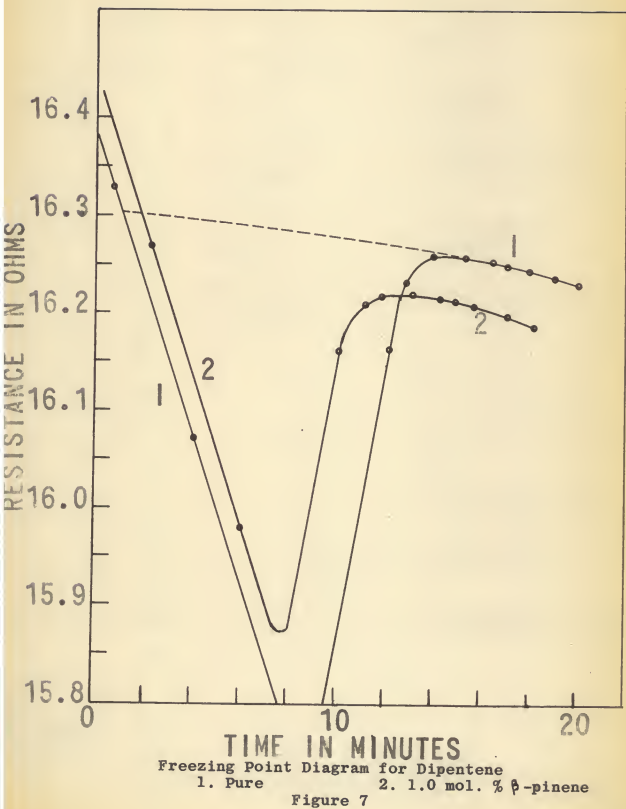


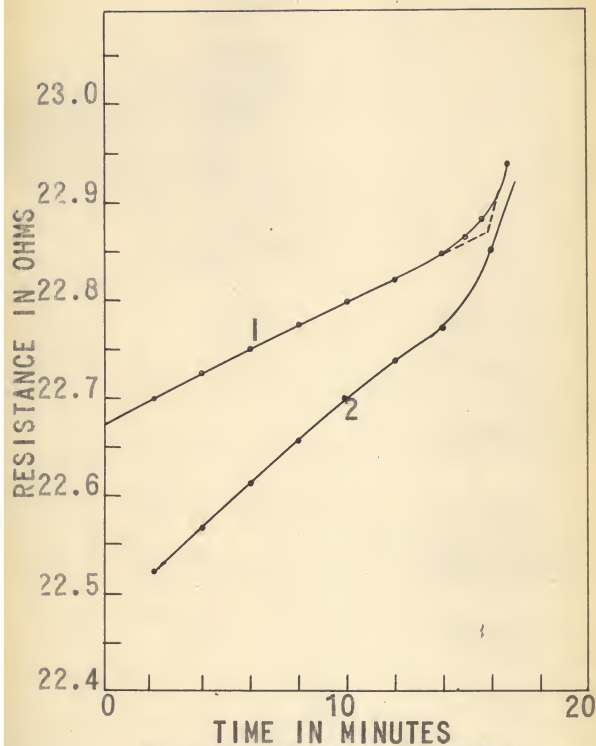
Freezing Point Diagram for d-Limonene

1. Pure

2. 0.4 mol.% α -pinene

Figure 6





Freezing Point Diagram for Allo-ocimene
1. Pure 2. 0.4 mol.% Dipentene

Figure 8

units, and X the calculated amount of impurity in mol. fraction units.

TABLE 11

FREEZING POINT DEPRESSIONS AND IMPURITIES

Compound	T _I Degrees	T _{II} Degrees	A mol. Fraction	X mol. Fraction
-pinene	0.52	1.45	0.010	0.004
d-Limonene	0.40	0.48	0.004	0.020
Dipentene	0.08	0.20	0.010	0.007
-pinene	0.18	0.31	0.010	0.013
Allo-ocimene	0.16	0.26	0.040	0.064

Except for allo-ocimene and d-limonene the amount of impurity in the sample is such that it will be negligible in effect on the heat of combustion. This is based on the fact that such impurities as are present will be isomers and as such will have nearly the same heats of combustion.

Allo-ocimene is known to exist as two geometric isomers.²⁶ These forms boil two degrees apart and therefore are difficult to separate by distillation. It is a safe assumption therefore that the impurity in the allo-ocimene is largely due to the effect of the trans form, which is present in smaller amounts than the cis form. For this reason, and because the heat of isomerization from the cis to the trans form

is not known, an uncertainty of 0.01 percent was added to the value of the heat of combustion of the allo-ocimene, on the assumption that the isomers differ in heats of combustion by less than 5 Kcal./mol.

d-Limonene appeared to be impure to the extent of 2.0 percent. It is not known what the nature of the impurity is but it is most likely isomeric with the d-limonene. An additional uncertainty of 0.01 percent was added to the value of the heat of combustion in this case also to make allowance for the impurity, for the reasons stated above.

Freezing Points.--From the data values of the freezing points of the compounds were estimated. Reported literature data appears to be grossly in error on this point, so that, although the values reported here are uncertain to the extent of several tenths of a degree they are believed to be a vast improvement on the values hitherto reported.

The freezing points were determined by extrapolating the equilibrium portion of the cooling curve back to the cooling curve of the liquid as shown in Figures 3 through 8. The values of resistances so determined were used in conjunction with the Callander conversion formula of the platinum thermometer to arrive at the freezing point of the compounds in degrees centigrade.

The data are listed in Table 12 together with literature values for the purposes of comparison.

TABLE 12

FREEZING POINTS OF THE COMPOUNDS

Compound	T_f	T_f
	Experimental	Literature
α -pinene	-75.51	-50 ²⁸
β -pinene	-61.54
d-Limonene	-75.03	-96.9 ²⁸
Dipentene	-39.03	-96.9 ²⁸
Allo-ocimene	-25.64	-21.0 ²⁹

CHAPTER V

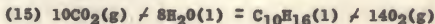
DISCUSSION OF RESULTS

The heats of combustion of β -pinene, allo-ocimene, and myrcene are here reported for the first time. Those of α -pinene, d-limonene, and dipentene have been determined before by Auwers, Roth, and Eisenlohr.³⁰ They give the following values: α -pinene 1480.6 Kcal./mol., d-limonene 1473.1 Kcal./mol., and dipentene 1462.0 Kcal./mol. The agreement between α -pinene and d-limonene in this investigation and the values previously reported for these compounds is surprisingly good. However, there is a large discrepancy in the values of dipentene. On the whole, it seems that the values reported previously should not be considered significant. The work was done some 40 years ago, before adequate standards had been established in calorimetry and before a good many of the errors inherent in the procedure had been analyzed. Also the degree of purity of the compounds formerly used is in doubt. It is therefore thought that the agreements shown are largely fortuitous and indicative of nothing in particular.

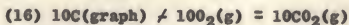
Heats of Formation from Combustion Data.--The obtaining of the data themselves was the primary object of the investigation. There are, however, some interesting energy relations that can be evaluated from the heats of combustion and other estimated thermodynamic properties. Since the heat

of formation of the compounds has more significance from a theoretical point of view, these will be calculated as a first step to point out the relations.

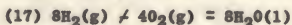
By means of the equations:



$$\Delta H = -\Delta H_{\text{C}} \text{ Kcal./mol.}$$

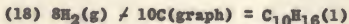


$$\Delta H = -940.5 \text{ Kcal./mol.}$$



$$\Delta H = -546.4 \text{ Kcal./mol.}$$

we can find the heat liberated in the reaction:



Adding together equations (15), (16), and (17) gives us equation (18) which is the reaction for the formation of the terpenes from their elements. The heat summation gives the relation $\Delta H_f = +\Delta H_{\text{C}} - 1486.9 \text{ Kcal./mol.}$ Values of the ΔH_{C} are listed in Table 10, p. 48. The heats of formation so determined are listed in Table 13, p. 66.

Heats of Formation from Bond Energies.—The heats of formation from bond energies were calculated from the following equations:

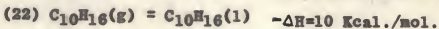
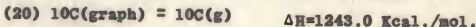
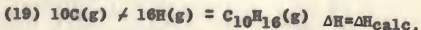


TABLE 13

HEATS OF FORMATION FROM COMBUSTION DATA

Compound	ΔH_f Kcal./mol.
β -pinene	- 1.5 \pm 0.34
α -pinene	- 3.6 \pm 0.25
Dipentene	-11.9 \pm 0.24
Allo-ocimene	- 5.8 \pm 0.43
d-Limonene	-12.7 \pm 0.27
Myrcene	- 3.8 \pm 0.24

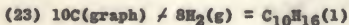
The structures of α -pinene, I, and β -pinene, II, are shown below.³¹



From this it can be seen that they have 10 C-C bonds, 1 C=C bond, and 16 C-H bonds. Using the values given by Pauling³² for the heat liberated in the formation of these bonds from the gaseous elements, we evaluated the heat liberated in equation (19). These values are 58.6 Kcal./mol. for a C-C bond, 100 Kcal./mol. for a C=C bond, and 87.3 Kcal./mol. for a C-H bond. The heat absorbed in equation (20) is 124.3

Kcal./mol.³² The heat absorbed in equation (21) is 103.4 Kcal./mol.³² Exact values of the heats of vaporization for most terpenes are not available*, so it is necessary to use some sort of approximation. Trouton's rule states that the entropy of vaporization for non-associated liquids is a constant at 21 cal./degree mol. The normal boiling points of the compounds vary between 430° and 455° K., so that the heat of vaporization at the normal boiling point was calculated as 9300 cal./mol. The heat of vaporization is somewhat higher at 298° K., so that a fairly good estimate of the heat evolved in equation (22) is 10 Kcal./mol. for all the compounds.

We now have all the information necessary to calculate the heat of formation of the compounds. If we add together equations (19), (20), (21), and (22), the sum is,



Denoting the heat calculated in equation (15) as $-\Delta H_{\text{calc.}}$, the heat of formation $\Delta H_f = -\Delta H_{\text{calc.}} + 2060.0$.

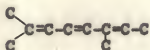
The structure of d-limonene and dipentene are the same since they are optical isomers. From their structure,³⁰ shown on p. 68, it is seen that there are 8 C-C bonds, 2

*Heats of vaporization for α -pinene and β -pinene have been determined in this laboratory to be about 11,140 and 10,390 cal./mol. respectively. See Armstrong, Vapor Pressures of α -pinene and β -pinene, University of Florida, (1943).

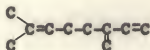
C=C bonds, and 16 C-H bonds.



The structures of allo-ocimene, I, and myrcene, II, are, ³⁰



I



II

It is seen that they have 6 C-C bonds, 3 C=C bonds, and 16 C-H bonds. Table 14, p. 69, gives the values of $\Delta H_{\text{calc.}}$ obtained for these compounds, the values of the heats of formation from the bond energies, and for the purposes of comparison the values of the heat of formation obtained from the heats of combustion.

Ring Strain in α -pinene and β -pinene.--Referring to Table 14, p. 69, we see that from the ΔH_f calculated from bond energies, α -pinene and β -pinene should be some 17.4 Kcal./mols. more stable than d-limonene. Actually, as shown in the last column, α -pinene and β -pinene are respectively, 9.1 and 11.2 Kcal./mols. less stable than d-limonene. A glance at the structures of these compounds on p. 66 will show the reason for this. The normal tetrahedral bonds of carbon have been strained considerably to form the cyclo-

TABLE 14

HEATS OF FORMATION FROM BOND ENERGIES

Compound	$\Delta H_{\text{calc.}}$ Kcal./mol.	ΔH_f Bond Energies Kcal./mol.	ΔH_f Heat of Combustion Kcal./mol.
α -pinene	2082.8	-22.8	- 3.6
β -pinene	2082.8	-22.8	- 1.5
d-Limonene	2065.4	- 5.4	-12.7
Dipentene	2065.4	- 5.4	-11.9
Myrcene	2048.0	/11.8	/ 3.8
Allo-ocimene	2048.0	/11.8	- 5.8

butane ring. This strained condition contributes to the instability of these compounds. The energy of the ring strain is 26.5 Kcal./mol. for α -pinene and 28.6 Kcal./mol. for β -pinene. These values are slightly higher than has been calculated before where an instability of some 20 Kcal./mol. was reported.³³ In the case of α -pinene and β -pinene there will be slightly more strain introduced than in a normal cyclobutane ring because of the six membered ring which must also be closed.

Resonance in Allo-ocimene and Myrcene.—The value of ΔH_f of allo-ocimene and myrcene calculated from the bond energies indicate that they should be 17.4 Kcal./mol. less

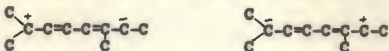
stable than d-limonene. ΔH_f values calculated from heats of combustion show that allo-ocimene is actually 79 Kcal./mol. less stable than d-limonene and that myrcene is actually 16.5 Kcal./mol. less stable than d-limonene.

Myrcene has two conjugated double bonds, which according to Pauling should stabilize it by about 6 Kcal./mol. due to resonance between the following forms:³²(and the one on p.68)



The actual value calculated here is 0.9 Kcal./mol.

Allo-ocimene has three double bonds, doubly conjugated. According to Pauling, resonance between forms such as these;



should stabilize it to the extent of about 10 Kcal./mol.

The actual value calculated here is 9.5 Kcal./mol.

Heats of Isomerization.--The compounds investigated undergo numerous isomerizations among themselves. In view of this it is of interest to calculate the heats of isomerization. In order to do this, d-limonene, being the most stable from the heats of formation, was chosen as the one to which the others were referred. The energy difference between it and the other isomers was calculated from the equation,

$$\text{C}_{10}\text{H}_{16}(1) = \text{C}_{10}\text{H}_{16}(\text{d-limonene})(1)$$

The values of the heats of isomerization so calculated are given below.

TABLE 15

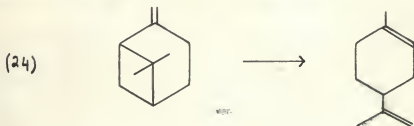
HEATS OF ISOMERIZATION

Compound	ΔH_1 Kcal./mol.
d-Limonene	0.00
Dipentene	$\neq 0.80$
Allo-ocimene	$\neq 6.40$
α -pinene	$\neq 9.10$
β -pinene	$\neq 11.20$
Myrcene	$\neq 16.50$

Entropies and Free Energies of Some Isomerization

Reactions.--Several reactions involving these compounds are of particular interest in that they are the products of thermal isomerization and, because of the ease with which they can be carried out, have been investigated extensively.

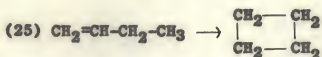
The isomerization of β -pinene to 1-limonene involves the breaking of a four membered ring.



$$\text{E. U.} - 262.8 = \text{cal/mol}$$

72

An estimate of the entropy change involved can be arrived at by considering the entropy change in the following reaction:



Parks and Huffman³⁴ have given the entropy of butene as $S^{298} = 67.3$ E. U., and have estimated the entropy of cyclobutane as $S^{298} = 44.0$ E. U. This gives ΔS^{298} for equation (25) as 23.3 E. U. No great error would be involved in assuming that this same entropy change occurred in reaction (24) above. Having values of the heat of isomerization and the entropy of isomerization we can calculate the value of the free energy of isomerization by the equation,

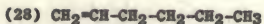
$$(26) \Delta F = \Delta H - T\Delta S$$

Then ΔF for equation (24) above is -18.1 Kcal./mol.

Considering now the reaction of β -pinene to myrcene



we see that in addition to the four membered ring being broken there is a rupture of the six membered ring and a conjugated pair of double bonds introduced. Proceeding in the same fashion as for the case of the four membered ring considered above we write the reaction:

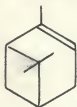


Parks and Huffman³⁴ give for the entropy of normal hexene, $S^{298} = 68.1$ E. U., and for the entropy of cyclohexane, $S^{298} = 49.2$. Then, making the same assumptions as before, the entropy change for reaction (28) is $\Delta S^{298} = 18.9$ E. U.

Equation (27) has, therefore, the entropy change involved in breaking the four membered ring plus that involved in breaking the six membered ring, minus 10.4 E. U. for formation of two conjugated double bonds,³⁵ or ΔS^{298} for equation (27) is 31.8 E. U. The value for the free energy change in equation (27) then becomes $\Delta F^{298} = -4.2$ Kcal./mol.

Considering the reactions for α -pinene to dipentene

(29)



and α -pinene to allo-ocimene



we see that the entropy change for reaction (29) should be the same as that for reaction (24), and the entropy change for reaction (30) should be the same as the reaction (27) except for a decrement in S due to 3 conjugated double bonds. Then utilizing the heats of isomerization and equation (26) we have for reaction (29), $\Delta F^{298} = -15.2$ Kcal./mol., and for reaction (30), $\Delta F^{298} = -8.6$ Kcal./mol.

Estimated Entropies of Formation of the Terpenes

Investigated.--As a step toward the evaluation of the free energies of formation of the compounds utilizing the heats of formation evaluated here, it is necessary to have values of the entropies of the compounds. These are estimated in the following manner:

We take as the base compound the hydrocarbon 2,6, dimethyl octane, $\text{CH}_3\text{-}\underset{\text{CH}_3}{\text{CH}}\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}\underset{\text{CH}_3}{\text{CH}}\text{-CH}_2\text{-CH}_3$.

Parks and Huffman³⁴ give as a general relation for calculating the entropy of branched chain hydrocarbons the formula,

$$S = 25 + 7.7n - 4.5r$$

where n is the number of carbon atoms in the compound and r is the number of methyl groups branched from the main chain. This formula gives for the entropy of the compound above 93.0 E. U.

Now myrcene is similar to this compound except that it has three double bonds, two of them conjugated. Klotz³⁵ says that 2.2 E. U. should be subtracted from the entropy of the base compound for each double bond introduced and that 10.4 E. U. should be subtracted from the entropy for each pair of conjugated double bonds. Making allowance for these contributions we get for the entropy of myrcene 76.0 E. U.

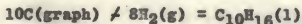
Allo-ocimene has the same number of double bonds, however they are all conjugated. This means that an additional 10.4 E. U. should be subtracted from the value arrived at above for myrcene. This gives a value for the entropy of allo-ocimene of 65.6 E. U.

d-Limonene and dipentene have the same structure. In order to form them from allo-ocimene, it is necessary to close a six membered ring. Another contribution enters from the fact that the conjugation in allo-ocimene is lost in the formation of d-limonene and dipentene. Therefore in going from allo-ocimene to d-limonene we lose 18.9 E. U. in forming the six membered ring and gain 20.8 E. U. in losing the double conjugation. This gives for the entropy of d-limonene and dipentene 67.5 E. U.

α -pinene and β -pinene can be formed from d-limonene by closing a four membered ring. As shown on p. 72, the entropy change in performing this operation is 23.3 E. U. Subtracting this from the entropy of d-limonene we get for the value of the entropy of α -pinene and β -pinene 44.2 E. U. respectively.

Estimated Free Energies of Formation.--Utilizing the values of the entropies of the compounds calculated above, it is possible to arrive at values of the free energies of formation of the compounds.

Using the equation



we can calculate the entropy change involved in the formation of the compounds. Parks and Huffman³⁴ give for the entropies of elemental carbon 1.3 E. U. per mole and for gaseous hydrogen 31.23 E. U. per mole. Then ΔS of formation equals $S(C_{10}H_{16}) - 262.8$.

The values of the entropies so determined are used with the values of the heats of formation in Table 13, p. 66, to give the values of the free energies of formation of the compounds.

The values of the entropies and the free energies are listed in Table 16, p. 77.

TABLE 16

ENTROPIES AND FREE ENERGIES OF FORMATION AT 25° C.

Compound	ΔS_f Cal./mol.	ΔF_f Kcal./mol.
α -pinene	-218.6	/61.5
β -pinene	-218.6	/63.6
d-Limonene	-195.3	/45.5
Dipentene	-195.3	/46.3
Myrcene	-186.8	/59.4
Allo-ocimene	-197.2	/53.0

TABLE 17

STEPS IN THE CALCULATION OF HEAT LIBERATED IN COMBUSTION OF BENZOIC ACID

Steps	Units	1	2	3	4	5
R20	Ohms	0.04627	0.97608	0.97643	0.00521	0.99498
R0	Ohms	0.03939	0.96648	0.96712	0.99660	0.98666
S10	Ohms/min.	0.000344	0.00048	0.000465	0.000430	0.000416
R56	Ohms	0.24952	0.18030	0.16893	0.19747	0.18778
R36	Ohms	0.25008	0.17813	0.16659	0.19497	0.18647
S46	Ohms/min.	-0.000028	0.00108	0.000117	0.000075	0.000065
S10 - S46	Ohms	0.00037	0.00038	0.00035	0.00034	0.000351
R46	Ohms	0.24986	0.17927	0.16777	0.19677	0.18714
R10	Ohms	0.04280	0.97132	0.97177	0.00092	0.99086
R46 - R10	Ohms	0.20706	0.20795	0.19600	0.19585	0.19628
k	Min. -1	0.00179	0.00178	0.00178	0.00173	0.00179
Rj	Ohms	0.22105	0.22044	0.21919	0.21936	0.20746
Rj - R46	Ohms	-0.02881	0.04717	0.05113	0.02259	0.02032
k(Rj - R46)	Ohms/min.	-0.000051	0.000084	0.000091	0.000039	0.000036
u	Ohms/min.	0.000024	0.00003	0.00003	0.000036	0.000029
ΔR dt	Ohms	0.00032	0.00039	0.00041	0.00057	0.00047
16Rj	Ohms min.	0.33181	0.34526	0.32215	0.31190	0.32253
-R25	Ohms min.	3.53680	3.62304	3.50560	3.50976	3.51936
-R25 R Δt	Ohms min.	1.20450	0.82950	0.77370	0.93390	0.88880
Area	Ohms min.	2.73644	1.93346	1.80676	2.13766	2.03517
k (Area) = K	Ohms min.	0.07233	1.20534	1.48394	0.75010	0.71792
HNO3	Ohms	-0.00013	0.00215	0.00222	0.00130	0.00128
Ign.	Ohms	0.00003	0.00004	0.00000	0.00000	0.00002
	Ohms	0.00022	0.00021	0.00021	0.00022	0.00016
ΔRc	Ohms	0.20331	0.19925	0.18740	0.18872	0.18956
ΔRc/CO2	Ohms/gm.	0.050113	0.050113	0.050091	0.050112	0.050095

TABLE 18

STEPS IN THE CALCULATION OF HEAT LIBERATED IN COMBUSTION OF β -PINENE

Steps	Units	1	2	3
R20	Ohms	0.96411	0.88729	0.99742
R0	Ohms	0.93394	0.87392	0.98800
S10	Ohms/min.	0.00050	0.000633	0.000471
R56	Ohms	0.15793	0.08702	0.18359
R36	Ohms	0.15498	0.08204	0.18138
S46	Ohms/min.	0.000147	0.000276	0.00011
S10 - S46	Ohms	0.15646	0.000357	0.000360
R46	Ohms	0.00036	1.08456	0.18250
R10	Ohms	0.95909	0.88033	0.99281
R46 - R10	Ohms	0.19737	0.20423	0.18969
k	Min. ⁻¹	0.00183	0.00175	0.00192
Rj	Ohms	0.22190	0.22130	0.22090
Rj - R46	Ohms	0.08544	0.13674	0.03840
k (Rj - R46)	Ohms/min.	0.000199	0.000239	0.000074
u	Ohms/min.	0.000028	0.000037	0.000037
v	Ohms	0.00045	0.00059	0.00059
$\frac{1}{k} \Delta R \cdot t$	Ohms min.	0.33333	0.32104	0.29177
$\frac{1}{k} R_j$	Ohms min.	3.55040	3.54080	3.53440
$\frac{1}{k} R_{25}$	Ohms min.	0.72690	0.35160	0.83910
$\frac{1}{k} R_{46}$	Ohms min.	1.68372	0.87133	1.96610
Area	Ohms min.	1.47311	2.63891	1.02097
k (Area) = K	Ohms	0.00270	0.00462	0.00196
HNO3	Ohms	0.00000	0.00000	0.00001
Ign.	Ohms	0.00027	0.00025	0.00027
ΔR_C	Ohms	0.18745	0.18929	0.18114
$\Delta R_C / CO_2$	Ohms/gm.	0.067488	0.067492	0.067488

TABLE 18--Continued

Steps	Units	4	5	6
R20	Ohms	0.03259	0.99696	0.00516
R0	Ohms	0.02460	0.98799	0.99547
S10	Ohms/min.	0.000399	0.000448	0.000455
R56	Ohms	0.22577	0.20644	0.20077
R36	Ohms	0.22535	0.20543	0.19913
S46	Ohms/min.	0.000021	0.000050	0.000082
S10 - S46	Ohms	0.00038	0.000390	0.000373
R46	Ohms	0.22563	0.20597	0.19997
R10	Ohms	0.02874	0.99254	0.00061
R46 - R10	Ohms	0.19689	0.21343	0.19936
k	Min. -1	0.00192	0.00193	0.00187
Rj	Ohms	0.22114	0.22110	0.22176
Rj - R46	Ohms	-0.00449	0.01513	0.02179
k (Rj - R46)	Ohms/min.	-0.000008	0.000029	0.000041
u	Ohms/min.	0.000029	0.000021	0.000413
V	Ohms	0.00047	0.00034	0.00066
$\frac{1}{V} \Delta R \cdot t$	Ohms min.	0.31456	0.33666	0.33597
162j	Ohms min.	3.53824	3.53760	3.54816
-225	Ohms min.	1.07820	0.97230	0.94855
$-\frac{1}{2} R_{tt}$	Ohms min.	2.46143	2.23919	2.17191
Area	Ohms min.	0.31317	0.66277	0.75367
k (Area) = X	Ohms	0.00060	0.00128	0.00141
RN03	Ohms	0.00002	0.00001	0.00001
I ga.	Ohms	0.00027	0.00027	0.00021
ΔR_c	Ohms	0.19140	0.20650	0.19168
$\Delta R_c / CO_2$	Ohms/ga.	0.67451	0.067451	0.067469

TABLE 19

STEPS IN THE CALCULATION OF HEAT LIBERATED IN COMBUSTION OF α -PINENE

Steps	Units	1	2	3	4	5
R ₂₀	Ohms	0.97124	0.96065	0.97563	0.97673	0.97021
R ₀	Ohms	0.96116	0.95142	0.96574	0.96697	0.95984
S ₁₀	Ohms/min.	0.000504	0.000511	0.000494	0.000488	0.000518
R ₅₆	Ohms	0.17188	0.17976	0.18085	0.21868	0.20806
R ₃₆	Ohms	0.16942	0.17763	0.17864	0.21817	0.20667
S ₄₆	Ohms/min.	0.000123	0.000106	0.000110	0.000035	0.000069
S ₁₀ - S ₄₆	Ohms	0.000401	0.000405	0.000384	0.000453	0.000449
R ₄₆	Ohms	0.17069	0.17869	0.17975	0.21853	0.20737
R ₁₀	Ohms	0.96633	0.95257	0.97075	0.97191	0.96506
R ₄₆ - R ₁₀	Ohms	0.20436	0.22312	0.20900	0.24662	0.24231
k	Min. ⁻¹	0.00185	0.00181	0.00184	0.00183	0.00185
R _j	Ohms	0.22190	0.22402	0.22162	0.22122	0.21509
R _j - R ₄₆	Ohms	0.05121	0.04533	0.04187	0.00269	0.00772
k (R _j - R ₄₆)	Ohms/min.	0.000095	0.000082	0.000770	0.000003	0.000014
u	Ohms/min.	0.000029	0.000024	0.000033	0.000030	0.000055
$\frac{1}{k} \Delta R \cdot t$	Ohms	0.00046	0.00039	0.00054	0.00049	0.00054
16R _j	Ohms min.	0.39692	0.3686	0.34591	0.36238	0.36659
-5R ₂₅	Ohms min.	3.55040	3.58432	3.54592	3.53952	3.44144
$\frac{1}{k} \Delta R$	Ohms min.	0.78450	0.84050	0.18405	1.03200	0.97900
Area	Ohms min.	1.83919	1.93439	1.94315	2.37891	2.35583
k (Area) = I	Ohms min.	1.32363	1.16629	1.10813	0.49199	0.47320
k (Area) = I	Ohms	0.00244	0.00211	0.00204	0.00090	0.00087
HNO ₃	Ohms	0.00001	0.00001	0.00001	0.00002	0.00003
Ign.	Ohms	0.00019	0.00024	0.00022	0.00027	0.00027
ΔR_c	Ohms	0.19508	0.21423	0.20022	0.23976	0.23450
$\Delta R_c / CO_2$	Ohms/gm.	0.067392	0.067368	0.067382	0.067369	0.067372

TABLE 20

STEPS IN THE CALCULATION OF HEAT LIBERATED IN COMBUSTION OF MYRCENE

Steps	Units	1	2	3	4	5
R20	Ohms	0.00438	0.99318	0.01639	0.00283	0.99208
R0	Ohms	0.99536	0.98563	0.00788	0.99404	0.98287
S10	Ohms/min.	0.000451	0.000477	0.000425	0.000439	0.000460
R56	Ohms	0.21298	0.21397	0.20094	0.19832	0.18386
R36	Ohms	0.21166	0.21254	0.19935	0.19673	0.18159
S46	Ohms/min.	0.000066	0.000071	0.000079	0.000079	0.000113
S10 - S46	Ohms	0.000385	0.000406	0.000035	0.000360	0.000347
R46	Ohms	0.21234	0.21312	0.20015	0.19753	0.18273
R10	Ohms	0.99995	0.99051	0.01221	0.99846	0.98753
R46 - R10	Ohms	0.21239	0.22361	0.18794	0.19907	0.19520
k	Min.-1	0.00181	0.00182	0.00184	0.00181	0.00178
Rj	Ohms	0.22900	0.23185	0.22820	0.23250	0.22644
Rj - R46	Ohms	0.01666	0.01873	0.02805	0.03497	0.04371
k (Rj - R46)	Ohms/min.	0.000030	0.000034	0.000052	0.000063	0.000060
u	Ohms/min.	0.000036	0.000037	0.000028	0.000016	0.000036
U	Ohms	0.00057	0.00060	0.00045	0.00026	0.00058
$\frac{1}{2} \Delta R \cdot t$	Ohms min.	0.33755	0.34326	0.29665	0.29058	0.32075
$\frac{1}{2} R j$	Ohms min.	3.66400	3.70960	3.65120	3.72000	3.62304
$-\frac{1}{2} R_{25}$	Ohms min.	1.00295	1.03115	0.94945	0.93475	0.85650
$-\frac{1}{2} R_{46}$	Ohms min.	2.30657	2.11198	2.17356	2.14396	1.98450
k (Area) = k	Ohms min.	0.69203	0.91473	0.82484	0.93187	1.10279
HNO ₃	Ohms	0.00126	0.00166	0.00152	0.00169	0.00196
Ign.	Ohms	0.00003	0.00001	0.00001	0.00002	0.00001
	Ohms	0.00027	0.00019	0.00027	0.00025	0.00027
ΔR_c	Ohms	0.20315	0.21490	0.18071	0.19168	0.18647
$\Delta R_c / CO_2$	Ohms/gm.	0.067695	0.067700	0.067709	0.067719	0.067724

TABLE 21

STEPS IN THE CALCULATION OF HEAT LIBERATED IN COMBUSTION OF ALLO-OCIMENE

Steps	Units	1	2	3	4	5
R ₂₀	Ohms	0.00766	0.00532	0.00838	0.99442	0.01426
R ₀	Ohms	0.99867	0.99656	0.00044	0.98544	0.00603
S ₁₀	Ohms/min.	0.000448	0.000438	0.000422	0.000449	0.000411
R ₅₆	Ohms	0.19525	0.20881	0.22394	0.22263	0.20056
R ₃₆	Ohms	0.19337	0.20772	0.22358	0.22217	0.19901
S ₄₆	Ohms/min.	0.000094	0.000054	0.000018	0.000023	0.000077
S ₁₀ - S ₄₆	Ohms	0.000354	0.000374	0.000404	0.000426	0.000334
R ₄₆	Ohms	0.19434	0.20829	0.22377	0.22241	0.19981
R ₁₀	Ohms	0.00321	0.00108	0.00482	0.99004	0.01004
R ₄₆ - R ₁₀	Ohms - 1	0.19113	0.20721	0.21895	0.23237	0.18977
k	Min.	0.00185	0.00180	0.00184	0.00183	0.00176
R ₁	Ohms	0.23265	0.22314	0.22079	0.22384	0.23010
R ₁ - R ₄₆	Ohms	0.03831	0.01485	0.00298	0.00143	0.03029
R ₁ (R ₁ - R ₄₆)	Ohms/min.	0.000071	0.000027	0.000006	0.000003	0.000053
u	Ohms/min.	0.000023	0.000028	0.000024	0.000020	0.000024
V	Ohms	0.00037	0.00044	0.00032	0.00038	0.00038
$\frac{\Delta R}{\Delta t}$	Ohms min.	0.31901	0.32313	0.33860	0.34941	0.32759
16R ₁	Ohms min.	3.72240	3.57024	3.53264	3.58144	3.63160
-5R ₂₅	Ohms min.	0.91870	0.99065	1.07925	1.05200	0.95360
$-\frac{1}{2} R_{46}$	Ohms min.	2.10702	2.26670	2.44265	2.42251	2.17225
Area	Ohms min.	1.01569	0.63602	0.34934	0.45634	0.88334
k (Area) = k	Ohms	0.00198	0.00114	0.00064	0.00083	0.00155
HNO ₃	Ohms	0.00001	0.00003	0.00001	0.00002	0.00002
Ign.	Ohms	0.00020	0.00027	0.00027	0.00027	0.00022
ΔR_c	Ohms	0.18325	0.20052	0.21340	0.22631	0.19258
$\Delta R_c / CO_2$	Ohms/gm.	0.067390	0.067286	0.067299	0.067332	0.067260

TABLE 22

STEPS IN THE CALCULATION OF HEAT LIBERATED IN COMBUSTION OF d-LIMONENE

Steps	Units	1	2	3	4
R20	Ohms	0.99796	0.99109	0.99050	0.01358
R0	Ohms	0.98960	0.98206	0.98113	0.00420
S10	Ohms/min.	0.000418	0.000451	0.000468	0.000469
R56	Ohms	0.20518	0.21192	0.23375	0.22572
R36	Ohms	0.20452	0.21095	0.23383	0.22482
S46	Ohms/min.	0.000033	0.000055	-0.000004	0.000045
S10 - S46	Ohms	0.000385	0.000396	0.000472	0.000424
R46	Ohms	0.20487	0.21152	0.23381	0.22527
R10	Ohms	0.99382	0.98659	0.98615	0.00895
R46 - R10	Ohms	0.21105	0.22493	0.24766	0.21632
k	Min.-1	0.00182	0.00176	0.00191	0.00196
Rj	Ohms	0.20882	0.22396	0.22700	0.24073
Rj - R46	Ohms	0.00395	0.01244	-0.00681	0.01546
k (Rj - R46)	Ohms/min.	0.000007	0.000022	-0.000013	0.000030
u	Ohms/min.	0.000026	0.000034	0.000017	0.000015
U	Ohms	0.00042	0.00054	0.00027	0.00024
$\frac{\Delta R}{k} \cdot t$	Ohms min.	0.30972	0.36111	0.40437	0.35154
16Rj	Ohms min.	3.34112	3.58336	3.63200	3.85168
-5R25	Ohms min.	0.97740	1.00420	1.11765	1.08270
- $\frac{1}{2} R_0$	Ohms min.	2.23549	2.30185	2.55567	2.45790
Area	Ohms min.	0.43759	0.63842	0.36300	0.66262
k (Area)=K	Ohms	0.00080	0.00112	0.00069	0.00130
HNO3	Ohms	0.00003	0.00003	0.00003	0.00003
Ign.	Ohms	0.00027	0.00027	0.00027	0.00027
ΔE_c	Ohms	0.20504	0.21776	0.24207	0.20941
$\Delta E_c/CO_2$	Ohms/gm.	0.067008	0.066988	0.066999	0.066998

TABLE 23

STEPS IN THE CALCULATION OF HEAT LIBERATED IN COMBUSTION OF DIPENTENE

Steps	Units	1	2	3
R20	Ohms	0.98920	0.99518	0.98480
R0	Ohms	0.98004	0.98627	0.97523
S10	Ohms/min.	0.000458	0.000445	0.000478
R56	Ohms	0.23025	0.22878	0.21894
R36	Ohms	0.21972	0.22836	0.21801
S46	Ohms/min.	0.000026	0.000021	0.000046
S10 - S46	Ohms	0.000432	0.000424	0.000432
R46	Ohms	0.22000	0.22858	0.21843
R10	Ohms	0.98477	0.99026	0.98012
R46 - R10	Ohms	0.23523	0.23832	0.23831
k	Min.-1	0.00183	0.00177	0.00181
Rj	Ohms	0.22705	0.22697	0.22820
Rj - R46	Ohms	0.00705	-0.00161	0.00997
k (Rj - R46)	Ohms/min.	0.000013	-0.000003	0.000018
u	Ohms/min.	0.000014	0.000024	0.000029
U	Ohms	0.00022	0.00038	0.00046
$\frac{1}{2} \Delta R \cdot t$	Ohms min.	0.38332	0.38535	0.38508
16Rj	Ohms min.	3.63280	3.63152	3.65120
-5R25	Ohms min.	1.04390	1.03285	1.04665
$-\frac{1}{2} R t$	Ohms min.	2.39740	2.49226	2.34262
A _{rea}	Ohms min.	0.57482	0.44176	0.64701
k (Area) = K	Ohms	0.00105	0.00078	0.00117
HNO3	Ohms	0.00003	0.00003	0.00003
I _{gn.}	Ohms	0.00027	0.00027	0.00025
ΔR_c	Ohms	0.22895	0.23172	0.23130
$\Delta R_c / CO_2$	Ohms/gm.	0.066958	0.066961	0.066975

SUMMARY

1. An apparatus for the determination of heats of combustion has been described in detail.
2. Measurements of the heats of combustion have been carried out on six terpene hydrocarbons.
3. The method of reducing the data has been described in detail.
4. Heats of formation have been evaluated from the heats of combustion and from bond energies and comparisons between them made.
5. Entropies of the compounds have been estimated empirically and from these values and the heats of formation calculated from heats of combustion, the free energies of formation estimated.
6. The free energy change of some isomerization reactions have been estimated.
7. The purity of the compounds has been estimated from measurements of the freezing range for five of the compounds investigated.
8. The freezing points of five of the compounds investigated have been reported.

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BIOGRAPHICAL NOTE

Warren T. Eriksen was born in New Port News, Virginia, on the 12th of August in 1923. He moved to Florida shortly thereafter, where he has lived since. He was educated in the public schools of Orange City and DeLand, Florida. In 1940 he enrolled in the University of Florida. From 1942 to 1946 he served in the United States Army, and on his return to the University of Florida took his B.S. in 1948. Since that time he has been in continuous enrollment in the Graduate School of the University of Florida, where he was a graduate assistant and later a teaching assistant.

COMMITTEE REPORT

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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